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(54) COATED POLYCARBONATE PLATE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polycarbonate plate with a transparent hard coat having no yellowing and no cloudiness even if it is used outdoor for a long period, surface defogging and antifouling properties.

SOLUTION: The coated polycarbonate plate is obtained by sequentially laminating a primer layer made of an organic resin containing an ultraviolet absorbent containing 20 wt.% or more of an effective volatile component, a silicone hard coating layer and a photocatalyst coating layer made of a silicone resin containing a metal oxide having a photocatalytic effect in this order.

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CLAIMS

[Claim(s)]

[Claim 1] The covering polycarbonate plate with which it comes to carry out the laminating of the photocatalyst coat which consists of silicon resin containing the metallic oxide which has the primer layer, the silicon rebound ace court layer, and the photocatalyst effectiveness it is ineffective on a polycarbonate plate from 20% of the weight or more of the ultraviolet ray absorbent and the organic resin of an effective nonvolatile matter in this sequence.

[Claim 2] The covering polycarbonate plate according to claim 1 whose ultraviolet ray absorbent in a primer layer is a benzophenone system.

[Claim 3] The covering polycarbonate plate according to claim 1 whose organic resin in a primer layer is the copolymer of an acrylic polymer, or an acrylic monomer and a meta-chestnut ROKISHI silane.

[Claim 4] the effective silicon component in a silicon rebound ace court layer — a silica and following type $R1dR2eSi(OR3)4-d-e$ — here R1 The alkyl group of the carbon atomic numbers 1-4, an alkyl halide radical, the aryl group of the carbon atomic numbers 6-12, or an aryl halide radical, The meta-chestnut ROKISHI alkyl group of the carbon atomic numbers 5-8, the ureido alkylene group of the carbon atomic numbers 2-10, They are an aromatic series ureido alkylene group, a halogenated-aromatics alkylene group, or a mercapto alkylene group. R2 The alkyl group of the carbon atomic numbers 1-6, an aryl group, an alkenyl radical, They are an alkyl halide radical or an aryl halide radical. R3 A hydrogen atom or the alkyl group of the carbon atomic numbers 1-4, the covering polycarbonate plate according to claim 1 which is an acyl group or an alkyl acyl group, and comes out and consists of a compound whose d is 1, 2, or 3, whose e is 0, 1, or 2, and which is expressed.

[Claim 5] The covering polycarbonate plate containing the compound which has the operation which eases this activity energy in order that a silicon rebound ace court layer may avoid the operation which the excessive activity energy of a photocatalyst coat which it has spreads, and promotes degradation of resin according to claim 1.

[Claim 6] The covering polycarbonate plate according to claim 5 which is the metal salt of the metal chelate compound whose structure where the compound which has the operation which eases activity energy is a chelate is aliphatic series, or an aliphatic series acid, and has compatibility in the matrix resin of a rebound ace court.

[Claim 7] The covering polycarbonate plate according to claim 5 with which the solution with which the compound which has the operation which eases activity energy contains it with an absorption peak at 400-550nm presents a purplish red color from blue.

[Claim 8] The covering polycarbonate plate according to claim 1 formed on the silicon rebound ace court layer to which corona treatment of the photocatalyst coat was carried out.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a covering polycarbonate plate. It is related with the polycarbonate plate which maintains fog resistance in more detail also at the time of an outdoor use, and does not have yellowing.

[0002]

[Description of the Prior Art] The covering polycarbonate goods which become the under coat list which the constituent which contains the copolymer of an acrylic monomer with (a) alkoxy silyl radical (meta) and alkyl (meta) acrylate, the (b) ammonium perchlorate, and the (c) ultraviolet ray absorbent in JP,2-274736,A hardened from the finishing coat which the colloidal silica content organopolysiloxane content constituent hardened and with which abrasion resistance and weatherability have been improved are indicated.

[0003] The compound of the inorganic compound which absorbs 0.1 - 30% of the weight of 320-400nm ultraviolet rays to the binder resin which is acrylic (meta) resin and/or vinyl system resin, and this binder resin as a primer constituent for silicon coating agents applied to the organic resin base material like a polycarbonate is indicated by JP,10-245521,A.

[0004] The polycarbonate resin laminate excellent in the weatherability of a polycarbonate plate which the whole surface was made to apply and harden a primer coating at least, was made to apply and harden a top coating subsequently to a it top, and was obtained is indicated by JP,11-58654,A. The above-mentioned primer coating consists 2, 2', and 4 and the benzophenone system ultraviolet ray absorbent containing a 4'-tetrahydro benzophenone per [8] nonvolatile matter 100 weight section of a coating - of 17 weight ***** thermosetting acrylics, and a top coating consists the above-mentioned ultraviolet ray absorbent of per [nonvolatile matter 100 weight section of a coating] 1 - 4 weight ***** colloidal silica content polyorganosiloxane.

[0005] Furthermore, the noise-proof wall which has a surface layer containing the particle of the photocatalyst like anatase mold titanium oxide, water-repellent silicone, and the matter, for example, the cobalt compound, for preventing the hydrophilization by optical pumping of said photocatalyst of this water-repellent silicone in the front face of the base material like a polycarbonate is indicated by JP,10-195829,A.

[0006] The hydrophilization method of the resin base material front face which carries out hydrophilization processing of the front face of the resin like acrylic resin, and covers the processed front face with the layer containing a photocatalyst and silicone resin, and consists of what the at least 1 section of the organic radical combined with the silicon atom of this silicone resin is permuted for by the hydroxyl group is indicated by JP,10-67873,A.

[0007] Finally, the building materials which have a paint film containing polyorganosiloxane and the inorganic particle which has a photocatalyst function on a front face are developed by JP,11-61044,A.

[0008] Degradation of the silicon resin which is matrix resin, and primer resin took place according to an operation of a photocatalyst, as a result, the crack occurred or exfoliated, and could not hold a photocatalyst paint film, but the resin base material deteriorated by ultraviolet rays, and when using it outdoors, what can discover sufficient weatherability was not known for the configuration of the conventional technique like the above.

[0009]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the covering polycarbonate plate equipped with the enveloping layer of a new configuration. Even if other purposes of this invention continue at a long period of time and it uses them outdoors, they are to offer the covering polycarbonate plate which can maintain fog resistance and moreover has neither yellowing nor cloudiness. The purpose and advantage of further others of this invention will become clear from the following explanation.

[0010]

[Means for Solving the Problem] According to this invention, the above-mentioned purpose and advantage of this invention are attained by the covering polycarbonate plate with which it comes to carry out the laminating of the photocatalyst coat which consists of silicon resin containing the metallic oxide which has the primer layer, the silicon rebound ace court layer, and the photocatalyst effectiveness it is ineffective on a polycarbonate plate from the organic resin containing 20% of the weight or more of the ultraviolet ray absorbent of an effective nonvolatile matter in this sequence.

[0011] A primer layer consists of 20% of the weight or more of the ultraviolet ray absorbent and the organic resin of an effective nonvolatile matter. As organic resin, it sticks to a polycarbonate plate and the resin in which a silicon rebound ace court and adhesion are possible is used. This organic resin is well-known, for example, can mention the copolymer of an acrylic polymer, and an acrylic monomer and a meta-chestnut ROKISHI silane, or the copolymer of an methacrylic monomer and an acrylic monomer with a benzotriazol radical or a benzophenone radical as a desirable thing. A copolymer with a meta-chestnut ROKISHI silane is [among these] still more desirable in an acrylic polymer and an acrylic monomer. The number of organic resin is one, or it can be used together two or more sorts.

[0012] Moreover, as an ultraviolet ray absorbent which a primer layer contains, a benzotriazol system and a benzophenone system can be mentioned as a desirable thing, for example. A benzophenone system is [among these] still more desirable. The number of ultraviolet ray absorbents is one, or two or more sorts, they can be mixed and can be used.

[0013] As a benzotriazol system ultraviolet ray absorbent For example, 2 -(2'- hydroxy-5'-methylphenyl)- Benzotriazol, 2 -(2'- hydroxy-3', 5'-G t-buthylphenyl)- Benzotriazol, 2 -(2'- hydroxy-5'-t-buthylphenyl)- Benzotriazol, 2 -(2'- hydroxy-5'-t-octyl phenyl)- Benzotriazol, 2-(2'- hydroxy-3', 5'-G t-buthylphenyl)-5-chloro-benzotriazol, Or the tinuvin 328 of tiba SUPESCHARUTI

KEMIKARUZU, Inc., tinuvin 384, tinuvin 900, tinuvin 928, and tinuvin 1130 can be mentioned.

[0014] as a benzophenone system ultraviolet ray absorbent — a — hydroxy-4-methoxybenzophenone, 2, 2', and 2, 4-dihydroxy benzophenone, 2-hydroxy-4-methoxybenzophenone, 2, and 2', 4', 4'-tetra-hydroxy benzophenone, and 2 and 2' — dihydroxy, -4 and 4' — dimethoxy benzophenone can be mentioned. Moreover, as an ultraviolet ray absorbent, the silane compound which, in addition to this, has benzotriazol or a benzophenone radical can also be used.

[0015] this ultraviolet ray absorbent — the effective non-volatile component in a primer layer — it contains at 20 – 50 % of the weight still more preferably 20 to 60% of the weight preferably 20% of the weight or more. A primer layer applies the solvent solution which contains an ultraviolet ray absorbent and organic resin by the specified quantity on a polycarbonate substrate, and is formed by removing and carrying out heat hardening of the solvent.

[0016] As a solvent, for example Ethylene glycol monomethyl ether acetate, Ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, Ethylene-glycol-monoethyl-ether acetate, propylene-glycol-monomethyl-ether acetate, Propylene glycol monoethyl ether acetate, propylene glycol monopropylether acetate, Propylene glycol monobutyl ether acetate, ethylene glycol wood ether, Ethylene glycol diethylether, ethylene glycol dipropyl ether, Ethylene glycol dibutyl ether, diethylene-glycol wood ether, Diethylene-glycol diethylether, diethylene-glycol dipropyl ether, Diethylene-glycol dibutyl ether, propylene glycol wood ether, Propylene glycol diethylether, propylene glycol monomethyl ether, The glycols like ethylene glycol monoethyl ether and ethylene glycol monobutyl ether; A cyclohexanone, The aliphatic series annular ketones like o-methylcyclohexanone, m-methylcyclohexanone, and p-methylcyclohexanone; Ethyl-acetate n-propyl acetate, The acetic ester like n-butyl acetate; the alcohols like a methanol, ethanol, 1-propanol, and 2-propanol and solvent naphtha, a methyl ethyl ketone, etc. can be mentioned.

[0017] Moreover, the above-mentioned solvent solution can contain the leveling agent of a hardening coat, and a lubricative grant agent as an arbitration component. As this **, the copolymer of polyoxyalkylene, the copolymer (paint additive 31 of Dow Corning) of poly dimethylsiloxane and polyoxyalkylene, and fluorocarbon is used preferably, for example. This ** is preferably used at 0.001 – 10 % of the weight to all volume. In addition, an anti-oxidant, a weatherproof grant agent, an antistatic agent, a bluing agent, etc. can also be contained as an arbitration component.

[0018] Solid content concentration is adjusted to 2 – 50% of the weight, and the above-mentioned solvent solution is used preferably. Spreading can be performed with a dip method, a Floe process, the spinner method, and a spray method.

[0019] As for spreading, it is desirable to carry out by thickness from which the thickness after hardening is set to 1–10 micrometers. If smaller than 1 micrometer, neither xanthochroism-proof nor weatherability is enough, and on the other hand, if larger than 10 micrometers, after giving the rebound ace court back, it becomes easy for a degree of hardness to fall. A solution paint film gives a primer layer after spreading by being heat-treated at the temperature of 100–120 degrees C for 15 minutes to several hours.

[0020] As for the covering polycarbonate plate of this invention, a silicon rebound ace court layer exists on a primer layer. The effective silicon component in a silicon rebound ace court layer It is here. desirable — a silica and following type R1dR2eSi(OR3)4-d-e — R1 The alkyl group of the carbon atomic numbers 1–4, an alkyl halide radical, the aryl group of the carbon atomic numbers 6–12, or an aryl halide radical, The meta-chestnut ROKISHI alkyl group of the carbon atomic numbers 5–8, the ureido alkylene group of the carbon atomic numbers 2–10, They are an aromatic series ureido alkylene group, a halogenated-aromatics alkylene group, or a mercapto alkylene group. R2 The alkyl group of the carbon atomic numbers 1–6, an aryl group, an alkenyl radical, it is an alkyl halide radical or an aryl halide radical, and R3 is a hydrogen atom or the alkyl group of the carbon atomic numbers 1–4, an acyl group, or an alkyl acyl group, and d is 1, 2, or 3, it comes out and e consists of a compound which is 0, 1, or 2 and which is expressed.

[0021] A silica can originate in the multiple oxide particle containing SiO2 in the colloidal silica (sol) which makes an active principle 10 – 50% of the weight of SiO2, or the range of 1–100nm particle size.

[0022] A multiple oxide is a composite of SiO2 and a metallic oxide, and can mention the oxide of one sort or two kinds or more of metals chosen from the group which consists of aluminum, Sn, Sb, Ta, Ce, La, Fe, Zn, W, Zr, In, and Ti as this metallic oxide, for example. As an example of a metallic oxide, aluminum 2O3, SnO2 and Sb 2O5, Ta2O5, CeO2 and La 2O3, Fe2O3, ZnO, WO3, ZrO2 and In 2O3, and TiO2 can be mentioned.

[0023] In order that said multiple oxide may raise the dispersibility to a solvent, surface treatment of it may be carried out with an organic silane compound. The amount of the organic silane compound used is 20 or less % of the weight preferably to multiple oxide particle weight. While the organic silane compound used for processing had had a hydrolysis radical, even if it carries out, surface treatment may be performed after hydrolyzing.

[0024] It is 3 SiX here. as this organic silane compound — the following formula R — It is here. the monofunctional nature silane which are the organic radical on which R has an alkyl group, a phenyl group, a vinyl group, a meta-chestnut ROKISHI radical, a sulfhydryl group, an amino group, or an epoxy group, and the radical which can hydrolyze X and which is come out of and expressed, and following formula R2SiX2 — It is here. the bifunctional silane as the above with the same definition of R and X come out of and expressed, and the following formula RSiX3 — the trifunctional silane and the following formula SiX4 as the above with the same definition of R and X which are come out of and expressed — the definition of X can mention the same tetrafunctional silane as the above come out of and expressed here.

[0025] As a monofunctional nature silane of the above-mentioned formula, for example Trimethylmethoxysilane, Triethylmethoxysilane, trimethylethoxysilane, triethylethoxysilane, Triphenylmethoxysilane, diphenylmethoxysilane, phenyldimethylmethoxysilane, Phenyldimethylethoxysilane, vinyldimethylmethoxysilane, A vinyl dimethylethoxy silane, gamma-acryloxypropyl dimethyl methoxysilane, gamma-methacryloxypropyl dimethyl methoxysilane, gamma-mercapto propyl dimethyl methoxysilane, gamma-mercapto propyl dimethylethoxy silane, N-beta(aminoethyl) gamma-aminopropyl dimethyl methoxysilane, gamma-aminopropyl dimethyl methoxysilane, gamma-aminopropyl dimethylethoxy silane, gamma-glycidoxy propyl dimethyl methoxysilane, gamma-glycidoxy PUOPIRUJI methoxyethoxy silane, and beta-(3,4-epoxycyclohexyl) ethyldimethylmethoxysilane can be mentioned.

[0026] As a bifunctional silane, for example Moreover, dimethyldimethoxysilane, Diethyldimethoxysilane, dimethyl diethoxysilane, diethyldiethoxysilane, Diphenyldimethoxysilane, phenylmethyldimethoxysilane, phenylmethyldiethoxysilane, Vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, gamma-acryloxypropylmethyldimethoxysilane, gamma-methacryloxypropyl dimethyldimethoxysilane, gamma-mercapto propylmethyldimethoxysilane, gamma-mercapto propylmethyldiethoxysilane, N-beta (aminoethyl) gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyldiethoxysilane, gamma-glycidoxy propyl methyldimethoxysilane, gamma-glycidoxy propyl methoxy diethoxysilane, and beta-(3,4-epoxycyclohexyl) ethyl methyl dimethoxysilane can be mentioned.

[0027] As a trifunctional silane, for example Moreover, methyl trimethoxysilane, Ethyltrimethoxysilane, methyl triethoxysilane, ethyltriethoxysilane, Phenyltrimethoxysilane, phenyltriethoxysilane, vinyltrimethoxysilane, Vinyltriethoxysilane, a vinyl (beta-methoxyethoxy) silane, gamma-acryloxypropyltrimethoxysilane, gamma-methacryloxypropyl trimethoxy silane, gamma-mercapto propyltrimethoxysilane, gamma-mercapto propyl triethoxysilane, N-beta (aminoethyl) gamma-aminopropyl trimethoxysilane, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-glycidoxypropyltrimethoxysilane, beta-glycidoxy propyltrimethoxysilane, gamma-glycidoxy propyltriethoxysilane, beta-glycidoxy propyltriethoxysilane, and beta-(3,4-epoxycyclohexyl) ethyltrimethoxysilane can be mentioned.

[0028] Furthermore, as a tetrafunctional silane, tetraethyl orthochromatic silicate and tetramethyl alt.silicate can be mentioned, for example. In case a multiple oxide is processed with this silane compound, it is desirable to carry out in water, alcohol, or other organic media.

[0029] As alcohol, for example A methanol, ethanol, isopropyl alcohol, The saturation fatty alcohol like n-butanol and 2-butanol; Methyl cellosolve, The cellosolves like ethylcellosolve, propyl cellosolve, and butyl cellosolve; Propylene glycol monomethyl ether, The propylene glycol monoethyl ether and the propylene glycol derivatives like propylene glycol monomethyl acetate; Methyl acetate, Ether like ethyl acetate, ester; diethylether like butyl acetate, and the methyl isobutyl ether; An acetone, The ketones like methyl isobutyl ketone; a xylene, the aromatic hydrocarbon; ethylene glycol like toluene, a tetrahydrofuran, N and N, - dimethylformamide, a dichloroethane, etc. can be mentioned.

[0030] Another effective silicon component of a silicon rebound ace court layer is a compound expressed with the above-mentioned formula.

[0031] As this compound, for example Trimethylmethoxysilane, triethylmethoxysilane, Trimethylethoxysilane, triethylethoxysilane, triphenylmethoxysilane, Diphenylmethoxysilane, phenyldimethylmethoxysilane, Phenyldimethylethoxysilane, vinyldimethylmethoxysilane, A vinyl dimethylethoxy silane, gamma-acryloxypropyl dimethyl methoxysilane, gamma-methacryloxypropyl dimethyl methoxysilane, gamma-mercapto propyl dimethyl methoxysilane, gamma-mercapto propyl dimethylethoxy silane, N-beta(aminoethyl) gamma-aminopropyl dimethyl methoxysilane, gamma-aminopropyl dimethyl methoxysilane, gamma-aminopropyl dimethylethoxy silane, gamma-glycidoxy propyl dimethyl methoxysilane, gamma-glycidoxy PUOPIRUJI methoxyethoxy silane, beta-(3,4-epoxycyclohexyl) ethyldimethylmethoxysilane dimethyldimethoxysilane, Diethyldimethoxysilane, dimethyl diethoxysilane, diethyldiethoxysilane, Diphenyldimethoxysilane, phenylmethyldimethoxysilane, phenylmethyldiethoxysilane, Vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, gamma-acryloxypropylmethyldimethoxysilane, gamma-methacryloxypropyl dimethyldimethoxysilane, gamma-mercapto propylmethyl dimethoxysilane, gamma-mercapto propylmethyl diethoxysilane, N-beta (aminoethyl) gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyldiethoxysilane, gamma-glycidoxy propyl methyldimethoxysilane, gamma-glycidoxy propyl methoxy diethoxysilane, beta-(3,4-epoxycyclohexyl) ethyl methyl dimethoxysilane, Methyl trimethoxysilane, ethyltrimethoxysilane, methyl triethoxysilane, Ethyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, Vinyltrimethoxysilane, vinyltriethoxysilane, a vinyl (beta-methoxyethoxy) silane, gamma-acryloxypropyltrimethoxysilane, gamma-methacryloxypropyl trimethoxy silane, gamma-mercapto propyltrimethoxysilane, gamma-mercapto propyl triethoxysilane, N-beta (aminoethyl) gamma-aminopropyl trimethoxysilane, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-glycidoxypropyltrimethoxysilane, beta-glycidoxy propyltrimethoxysilane, gamma-glycidoxy propyltriethoxysilane, beta-glycidoxy propyltriethoxysilane, beta-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, tetraethyl orthochromatic silicate, and tetramethyl orthochromatic silicate can be mentioned.

[0032] As dispersion liquid in a liquid medium which contain the effective silicon component like the above by the specified quantity, a silicon rebound ace court layer is applied on a primer layer, and a liquid medium is removed and it is formed by carrying out heat hardening.

[0033] As a liquid medium, for example Ethylene glycol monomethyl ether acetate, Ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, Ethylene-glycol-monobutyl-ether acetate, propylene-glycol-monomethyl-ether acetate, Propylene glycol monoethyl ether acetate, propylene glycol monopropylether acetate, Propylene glycol monobutyl ether acetate, ethylene glycol wood ether, Ethylene glycol diethylether, ethylene glycol dipropyl ether, Ethylene glycol dibutyl ether, diethylene-glycol wood ether, Diethylene-glycol diethylether, diethylene-glycol dipropyl ether, Diethylene-glycol dibutyl ether, propylene glycol wood ether, Propylene glycol diethylether, propylene glycol monomethyl ether, The glycols like ethylene glycol monoethyl ether and ethylene glycol monobutyl ether; A cyclohexanone, The aliphatic series annular ketones like o-methylcyclohexanone, m-methylcyclohexanone, and p-methylcyclohexanone; Ethyl-acetate n-propyl acetate, The acetic ester like n-butyl acetate; the alcohols like a methanol, ethanol, 1-propanol, and 2-propanol can be mentioned.

[0034] In the above-mentioned dispersion liquid, the curing catalyst of a rebound ace court layer usually contains. As a curing catalyst, the alkali-metal salt of a carboxylic acid and ammonium salt, the metal salt of an acetylacetone and ammonium salt, the metal salt of ethyl acetoacetate and an acetylacetone and the metal salt which ethyl acetoacetate configured, the 1st - tertiary amine, a polyalkylene amine, sulfonate, magnesium perchlorate, an ammonium perchlorate, etc. can be mentioned, for example. These compounds can also be used together with an organic mercaptan or a mercapto alkylene silane.

[0035] As an example of the above-mentioned metal salt, salts with the chelate compound or aliphatic series acid containing the following core metal can be mentioned. The central metal like aluminum, Zr, Co, Zn, Sn, Mn, V, Cu, Ce, Cr, Ru, Ga, Cd, and Fe; An acetylacetone, G n-butoxide-monochrome-ethyl Acetate, G n-butoxide-monochrome-methyl Chelate compound; like acetate, methylethyl ketoxime, 2, 4-hexane dione, 3, 5-heptane dione, and the aceto oxime And the aliphatic series acid compound like a 2-ethyl-hexyl acid, stearin acid, a lauric acid, oleic acid, an acetic acid, a sebacic acid, dodecane diacid, a propionic acid, a brasylic acid, an isobutyl acid, and a citraconic acid.

[0036] As an example of the 1st - the 3rd amine, moreover, fatty amine, aromatic amine, An amino silane etc. is desirable. For example, polymethylene diamine, polyether diamine, Diethylenetriamine, iminobis propylamine, bis-hexamethylene triamine, Diethylenetriamine, a tetra-ethylene PENTA amine, a pentaethylene hexa amine, Pentaethylenhexamine, dimethylamino propylamine, aminoethylethanolamine, Methyliminobispropylamine, menthonaphtene diamine, N-friend NOMECHI ruby perazine, 1, 3-diamino cyclohexane, isophorone diamine, meta-xylene diamine, Tetra-chloro paraxylene diamine, meta-phenylenediamine, 4, and 4'-methylenedianiline, Diamino diphenyl sulfone, a benzidine, a toluidine, diamino diphenyl ether, - thio dianiline, and 4 and 4' 4, 4'-screw (ortho toluidine) dianisidine, o-phenylenediamine, 2, 4-toluene diamine, methylenebis (o-chloroaniline), JIAMINIJI tolyl sulfone, screw (3, 4-diamino phenyl) sulfone, 2, 6-diamino pyridine, a 4-chloro-o-phenylenediamine, A 4-methoxy-6-methyl-m-phenylenediamine, m-amino benzylamine, N, N, N', N'- tetramethyl-1, 3-butanediamine, N and N, N', N'-tetramethyl-p-phenylene diamine, Tetramethyl guanidine, triethanolamine, a 2-dimethylamino-2-hydroxy propane, N, - dimethyl piperazine, and N'N, N' screw

[-] [(2-hydroxy) propyl] piperazine, N-methyl HORUMORIN, a hexamethylenetetramine, a pyridine, pyrazine, A quinoline, benzyl dimethylamine, alpha-methylbenzyl monomethylamine, 2-(dimethyl aminomethyl) phenol, 2 and 4, 6-tris (dimethylamino methylol) phenol, N-methyl piperazine, a pyrrolidine, HORUMORIN, N-beta (aminoethyl) gamma-aminopropyl trimethoxysilane, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, N-beta(aminoethyl) gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, and gamma-aminopropyl methyldiethoxysilane can be mentioned.

[0037] The curing catalyst like the above can be added also in the time of preparation of dispersion liquid just before spreading. The rate of a curing catalyst is 0.001 - 10 % of the weight preferably to the effective formed element in dispersion liquid.

[0038] In order to avoid the operation which the excessive activity energy which the photocatalyst coat which mentions the above-mentioned dispersion liquid for a silicon rebound ace court layer later in this invention has spreads, and promotes degradation of resin, it is desirable to contain the compound which has the operation which eases this activity energy.

[0039] As this compound, the metal chelate compound whose structure of a chelate is aliphatic series, for example, and the compound of an aliphatic series acid metal salt are desirable, and what has compatibility in the matrix resin of a rebound ace court layer is still more desirable.

[0040] As a central metal of this compound, Co, Mn, V, Cu, Ce, Cr, Ru, Ga, Cd, and Fe can be mentioned, for example. Moreover, as a chelate compound, they are an acetylacetone and G n-butoxide-monochrome-ethyl, for example. Acetate, G n-butoxide-monochrome-methyl Acetate, methylethyl ketoxime, 2, 4-hexane dione, 3, and 5-heptane dione and the aceto oxime can be mentioned. Furthermore, as an aliphatic series acid compound, a 2-ethyl-hexyl acid, stearin acid, a lauric acid, oleic acid, an acetic acid, a sebacic acid, dodecane diacid, a propionic acid, a brasylic acid, an isobutyl acid, and a citraconic acid can be mentioned, for example. That to which the solution containing it presents a purplish red color from blue with an absorption peak is desirable to 400-550nm of these compounds.

[0041] This compound is preferably used at 0.001 - 5 % of the weight to the solid content in dispersion liquid. The effectiveness which used this compound when fewer than 0.001 % of the weight is hardly acquired, but when [than 5 % of the weight] more [again], the degree of hardness of a rebound ace court layer tends to deteriorate.

[0042] Moreover, the above-mentioned dispersion liquid can contain the leveling agent of a hardening coat, and a lubricative grant agent as an arbitration component. As this **, the copolymer of polyoxalkylene, the copolymer (paint additive 31 of Dow Corning) of poly dimethylsiloxane and polyoxalkylene, and fluorocarbon is used preferably, for example. This ** is preferably used at 0.001 - 10 % of the weight to all volume. In addition, an anti-oxidant, a weatherproof grant agent, an antistatic agent, a bluing agent, etc. can also be contained as an arbitration component.

[0043] Solid content concentration is adjusted to 2 - 50% of the weight, and the above-mentioned dispersion liquid are used preferably. Spreading can be performed with a dip method, a Floe process, the spinner method, and a spray method.

[0044] As for spreading, it is desirable to carry out by thickness from which the thickness after hardening is set to 2-7 micrometers. If smaller than 2 micrometers, a degree of hardness is not enough, and on the other hand, if larger than 7 micrometers, it will become easy to generate a crack in a rebound ace court layer. A dispersion-liquid paint film gives a silicon rebound ace court layer after spreading by being heat-treated at the temperature of 100-130 degrees C for 1 to 24 hours.

[0045] The covering polycarbonate plate of this invention has a photocatalyst coat further on a silicon rebound ace court layer. This layer consists of silicon resin containing the metallic oxide which has the photocatalyst effectiveness. The metallic-oxide particle which generates the band gap which discovers the photocatalyst effectiveness by UV irradiation as a metallic oxide which has the photocatalyst effectiveness is desirable. As this particle, TiO₂, TiO₃, SrTiO₃, FeTiO₃, WO₃, SnO₂, Bi₂O₃, In₂O₃, ZnO and Fe₂O₃, RuO₂, CdO and CdS, CdSe, GaP, GaAs, CdFeO₃ and MoS₂, and LaRhO₃ grade can be mentioned, for example. It is TiO₂ and ZnO preferably and is the anatase mold TiO₂ especially preferably.

[0046] moreover, following type: R₁dR₂eSi(OR₃)_{4-d-e} which indicated the silicon rebound ace court layer as silicon resin — it is here and the definition of R₁, R₂, R₃, d, and e can mention the hardened material of the same compound as the above come out of and expressed as a desirable thing.

[0047] The same thing as what indicated the rebound ace court etc. also as a curing catalyst and a liquid medium can be used. As a liquid medium, 1-propanol is desirable especially here. As for the coating liquid for a photocatalyst coat, it is desirable that solid content concentration is 1 - 10 % of the weight.

[0048] Spreading can be performed with a dip method, a Floe process, the spinner method, and a spray method. As for spreading, it is desirable to carry out by thickness from which the thickness after hardening is set to 5-50nm. If larger than 50nm, the film will become cloudy, and the interference color is not visible and desirable. A solution paint film gives a photocatalyst coat after spreading by being heat-treated at the temperature of 100-130 degrees C for 1 to 5 hours.

[0049] As for a photocatalyst coat, it is desirable to prepare on the silicon rebound ace court layer which carried out corona treatment. A photocatalyst coat is joined still more strongly in a silicon rebound ace court layer by it. Moreover, a photocatalyst coat can be made to contain the compound which has the operation which eases this activity energy in order to avoid the operation which the excessive activity energy which the compound, i.e., a photocatalyst layer, which indicated the rebound ace court layer has spreads, and promotes degradation of resin.

[0050] The covering polycarbonate plate of this invention can be used for a sound-proof wall, a grading application, and an inside-of-a-house application.

[0051]

[Effect of the Invention] According to this invention the above-mentioned passage, a polycarbonate plate with a transparence rebound ace court with the surface fog resistance and antifouling property which there is no yellowing even if it uses it outdoors over a long period of time, and cloudiness does not have, either can be offered.

[0052]

[Example] Hereafter, this invention is further explained in full detail according to an example. The various matter used in the example is as follows.

Polycarbonate plate: The plate (1mx30cmx5mm) with a PORIKA ace (product made from Plastics In cylinder) thickness of 5mm was used.

[0053] Primer 1: They are 850g and Dow in the copolymer (Mn=10000, Mw=40000) of 4:1 at the mole ratio of methyl methacrylate and methacryloxy propyl trimethoxysilane aboutg [100], 2, and 4-dihydroxy benzophenone 50g and propylene glycol monomethyl ether. Solution which consists the Corning paint additive 31 of 0.1g.

[0054] primer 2: — acryloid A-10S (acrylic resin by loam & Haas) — 100g, 2, 2', 4, and 4' - tetra-hydroxy benzophenone 40g and propylene glycol monomethyl ether — 860g and Dow Solution which consists the Corning paint additive 31 of 0.1g.

[0055] Rebound ace court 1: Snow tex 0-40 (the product made from the Nissan chemistry: colloidal silica, moisture powder, 40% of nonvolatile matters) Isopropyl alcohol 648g, 2g of sodium acetate, Dow after making 150g and methyl trimetoxysilane 200g react Solution which added 0.1g for the Corning paint additive 31.

[0056] Rebound ace court 2: Snow tex 0-40 (the product made from the Nissan chemistry: colloidal silica, moisture powder, 40% of nonvolatile matters) 2 and 4-dihydroxy benzophenone 20g, isopropyl alcohol 628g, 2g of sodium acetate, Dow after making 150g and methyl trimetoxysilane 200g react Solution which consists the Corning paint additive 31 of 0.1g.

[0057] Rebound ace court 3: Snow tex 0-40 (the product made from the Nissan chemistry: colloidal silica, moisture powder, 40% of nonvolatile matters) They are 0.1g, 2g of sodium acetate, and Dow about isopropyl alcohol after making 150g and methyl trimetoxysilane 200g react 647g, and Co(II) acetylacetone 2 hydrate. Solution which added 0.1g of Corning paint additives 31.

[0058] The solution containing TiO₂: The solution which consists ST-K03 (the Ishihara Sangyo make, 10% of nonvolatile matters) of 50wt(s)% and 1-propyl alcohol 50wt%.

[0059] Moreover, the conditions and the various examining methods which were used in the example, such as the method of application, are as follows.

[0060] Method of application: A flow coat or a DIP coat.

Corona-treatment conditions: Output 500W, the irradiation range of 5mm, processing during 3 minutes.

Rebound-ace-court hardening conditions: It is 60 minutes at 120 degrees C.

The hardening conditions of the solution containing TiO₂: It is 120 degrees C and is 30 to 60 minutes.

[0061] Adhesion: Go board trial JIS It is based on K5400.

Whenever [yellow]: JIS It measures according to K7103.

Hardness: JIS It is too heavy 500g at the Taber abrasion test based on K7204, and the turbidity before and behind 500 rotations is measured.

Turbidity: JIS It is based on K7105.

An early contact angle: Measure a contact angle with 0.1 cc waterdrop after irradiating the light source of 2 the ultraviolet-rays reinforcement of 0.5mW/cm for 3 hours.

The contact angle after a weathering test: Measure a contact angle with 0.1 cc waterdrop.

[0062] Weatherability 1: Evaluate the appearance of 3000 hours after, and adhesion using a sunshine carbon arc weatherometer weatherability accelerated test machine (the black panel temperature of 63 degrees C and a water spray are sprayed for 12 minutes per hour).

[0063] The primer 1 was carried out in the flow coat, spreading hardening of the rebound ace court 1 was carried out in the flow coat at the example 1 polycarbonate plate after spreading hardening (1.8-3.5 micrometers in thickness of the primer layer after hardening) (2-5 micrometers in thickness of the rebound ace court layer after hardening), spreading hardening of the solution which contains the corona treatment back TiO₂ further was carried out, and thickness of the photocatalyst coat after hardening was set to 20-40nm.

[0064] Example 2 primer 2 was carried out in the flow coat, spreading hardening of the rebound ace court 2 was carried out in the flow coat after spreading hardening (1-2 micrometers in thickness after hardening) (2-5.5 micrometers of thickness of the rebound ace court layer after hardening), spreading hardening of the solution containing the corona treatment back TiO₂ was carried out, and thickness of the photocatalyst coat after hardening was set to 20-40nm.

[0065] Example 3 primer 1 is applied on a DIP coat (a part for 1.5m/in raising rate). At 115 degrees C, after hardening during 30 minutes (1.8-3.5 micrometers in thickness of the primer layer after hardening), The rebound ace court 3 was applied on the DIP coat (a part for 1.5m/in raising rate), it hardened for 60 minutes at 120 degrees C (thickness of 2-5 micrometers of the rebound ace court layer after hardening), spreading strengthening of the solution containing the corona treatment back TiO₂ was carried out, and thickness of the photocatalyst coat after hardening was set to 20-40nm.

[0066] The process after corona treatment was not carried out in example of comparison 1 example 1, but others were performed similarly to an example 1.

[0067] In example of comparison 2 example 1, the process which carries out spreading hardening of the rebound ace court 1 was not carried out, but others were performed similarly to an example 1. The result was shown in Table 1 and 2.

[0068]

[Table 1]

項目	初期性能				
	密着性	硬度	ヘイズ率	YI	初期接触角
実施例1	100%	2%	0.5%	-1.0	1°
実施例2	100%	4%	0.6%	0.1	1°
実施例3	100%	2%	0.6%	-1.5	1°
比較例1	100%	2%	0.2%	-1.0	85°
比較例2	100%	20%	0.4%	0.8	2°

[0069]

[Table 2]

項目	耐候性試験後				
	密着性	硬度	ヘイズ率	YI	接触角
実施例1	100%	4%	1%	1.0	6°
実施例2	100%	8%	2%	2.0	8°
実施例3	100%	4%	1%	0.5	3°
比較例1	100%	5%	1%	1.5	72°
比較例2	0%	20%	10%	18%	55°

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TECHNICAL FIELD

[Field of the Invention] This invention relates to a covering polycarbonate plate. It is related with the polycarbonate plate which maintains fog resistance in more detail also at the time of an outdoor use, and does not have yellowing.

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PRIOR ART

[Description of the Prior Art] The covering polycarbonate goods which become the under coat list which the constituent which contains the copolymer of an acrylic monomer with (a) alkoxy silyl radical (meta) and alkyl (meta) acrylate, the (b) ammonium perchlorate, and the (c) ultraviolet ray absorbent in JP,2-274736,A hardened from the finishing coat which the colloidal silica content organopolysiloxane content constituent hardened and with which abrasion resistance and weatherability have been improved are indicated.

[0003] The compound of the inorganic compound which absorbs 0.1 - 30% of the weight of 320-400nm ultraviolet rays to the binder resin which is acrylic (meta) resin and/or vinyl system resin, and this binder resin as a primer constituent for silicon coating agents applied to the organic resin base material like a polycarbonate is indicated by JP,10-245521,A.

[0004] The polycarbonate resin laminate excellent in the weatherability of a polycarbonate plate which the whole surface was made to apply and harden a primer coating at least, was made to apply and harden a top coating subsequently to a it top, and was obtained is indicated by JP,11-58654,A. The above-mentioned primer coating consists 2, 2', and 4 and the benzophenone system ultraviolet ray absorbent containing a 4'-tetrahydro benzophenone per [8] nonvolatile matter 100 weight section of a coating - of 17 weight ***** thermosetting acrylics, and a top coating consists the above-mentioned ultraviolet ray absorbent of per [nonvolatile matter 100 weight section of a coating] 1 - 4 weight ***** colloidal silica content polyorganosiloxane.

[0005] Furthermore, the noise-proof wall which has a surface layer containing the particle of the photocatalyst like anatase mold titanium oxide, water-repellent silicone, and the matter, for example, the cobalt compound, for preventing the hydrophilization by optical pumping of said photocatalyst of this water-repellent silicone in the front face of the base material like a polycarbonate is indicated by JP,10-195829,A.

[0006] The hydrophilization method of the resin base material front face which carries out hydrophilization processing of the front face of the resin like acrylic resin, and covers the processed front face with the layer containing a photocatalyst and silicone resin, and consists of what the at least 1 section of the organic radical combined with the silicon atom of this silicone resin is permuted for by the hydroxyl group is indicated by JP,10-67873,A.

[0007] Finally, the building materials which have a paint film containing polyorganosiloxane and the inorganic particle which has a photocatalyst function on a front face are developed by JP,11-61044,A.

[0008] Degradation of the silicon resin which is matrix resin, and primer resin took place according to an operation of a photocatalyst, as a result, the crack occurred or exfoliated, and could not hold a photocatalyst paint film, but the resin base material deteriorated by ultraviolet rays, and when using it outdoors, what can discover sufficient weatherability was not known for the configuration of the conventional technique like the above.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention the above-mentioned passage, a polycarbonate plate with a transparence rebound ace court with the surface fog resistance and antifouling property which there is no yellowing even if it uses it outdoors over a long period of time, and cloudiness does not have, either can be offered.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the covering polycarbonate plate equipped with the enveloping layer of a new configuration. Even if other purposes of this invention continue at a long period of time and it uses them outdoors, they are to offer the covering polycarbonate plate which can maintain fog resistance and moreover has neither yellowing nor cloudiness. The purpose and advantage of further others of this invention will become clear from the following explanation.

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MEANS

[Means for Solving the Problem] According to this invention, the above-mentioned purpose and advantage of this invention are attained by the covering polycarbonate plate with which it comes to carry out the laminating of the photocatalyst coat which consists of silicon resin containing the metallic oxide which has the primer layer, the silicon rebound ace court layer, and the photocatalyst effectiveness it is ineffective on a polycarbonate plate from the organic resin containing 20% of the weight or more of the ultraviolet ray absorbent of an effective nonvolatile matter in this sequence.

[0011] A primer layer consists of 20% of the weight or more of the ultraviolet ray absorbent and the organic resin of an effective nonvolatile matter. As organic resin, it sticks to a polycarbonate plate and the resin in which a silicon rebound ace court and adhesion are possible is used. This organic resin is well-known, for example, can mention the copolymer of an acrylic polymer, and an acrylic monomer and a meta-chestnut ROKISHI silane, or the copolymer of a methacrylic monomer and an acrylic monomer with a benzotriazol radical or a benzophenone radical as a desirable thing. A copolymer with a meta-chestnut ROKISHI silane is [among these] still more desirable in an acrylic polymer and an acrylic monomer. The number of organic resin is one, or it can be used together two or more sorts.

[0012] Moreover, as an ultraviolet ray absorbent which a primer layer contains, a benzotriazol system and a benzophenone system can be mentioned as a desirable thing, for example. A benzophenone system is [among these] still more desirable. The number of ultraviolet ray absorbents is one, or two or more sorts, they can be mixed and can be used.

[0013] As a benzotriazol system ultraviolet ray absorbent For example, 2-(2'-hydroxy-5'-methylphenyl)-Benzotriazol, 2-(2'-hydroxy-3', 5'-G t-buthylphenyl)-Benzotriazol, 2-(2'-hydroxy-5'-t-buthylphenyl)-Benzotriazol, 2-(2'-hydroxy-5'-t-octylphenyl)-Benzotriazol, 2-(2'-hydroxy-3', 5'-G t-buthylphenyl)-5-chloro-benzotriazol, Or the tinuvin 328 of tiba SUPESCHARUTI KEMIKARUZU, Inc., tinuvin 384, tinuvin 900, tinuvin 928, and tinuvin 1130 can be mentioned.

[0014] as a benzophenone system ultraviolet ray absorbent — a - hydroxy-4-methoxybenzophenone, 2, 2', and 2, 4-dihydroxy benzophenone, 2-hydroxy-4-methoxybenzophenone, 2, and 2 '4, 4'-tetra-hydroxy benzophenone, and 2 and 2 — ' - dihydroxy -4 and 4' - dimethoxy benzophenone can be mentioned. Moreover, as an ultraviolet ray absorbent, the silane compound which, in addition to this, has benzotriazol or a benzophenone radical can also be used.

[0015] this ultraviolet ray absorbent — the effective non-volatile component in a primer layer — it contains at 20 - 50 % of the weight still more preferably 20 to 60% of the weight preferably 20% of the weight or more. A primer layer applies the solvent solution which contains an ultraviolet ray absorbent and organic resin by the specified quantity on a polycarbonate substrate, and is formed by removing and carrying out heat hardening of the solvent.

[0016] As a solvent, for example Ethylene glycol monomethyl ether acetate, Ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, Ethylene-glycol-monobutyl-ether acetate, propylene-glycol-monomethyl-ether acetate, Propylene glycol monoethyl ether acetate, propylene glycol monopropylether acetate, Propylene glycol monobutyl ether acetate, ethylene glycol wood ether, Ethylene glycol diethylether, ethylene glycol dipropyl ether, Ethylene glycol dibutyl ether, diethylene-glycol wood ether, Diethylene-glycol diethylether, diethylene-glycol dipropyl ether, Diethylene-glycol dibutyl ether, propylene glycol wood ether, Propylene glycol diethylether, propylene glycol monomethyl ether, The glycols like ethylene glycol monoethyl ether and ethylene glycol monobutyl ether; A cyclohexanone, The aliphatic series annular ketones like o-methylcyclohexanone, m-methylcyclohexanone, and p-methylcyclohexanone; Ethyl-acetate n-propyl acetate, The acetic ester like n-butyl acetate; the alcohols like a methanol, ethanol, 1-propanol, and 2-propanol and solvent naphtha, a methyl ethyl ketone, etc. can be mentioned.

[0017] Moreover, the above-mentioned solvent solution can contain the leveling agent of a hardening coat, and a lubricative grant agent as an arbitration component. As this **, the copolymer of polyoxyalkylene, the copolymer (paint additive 31 of Dow Corning) of poly dimethylsiloxane and polyoxyalkylene, and fluorocarbon is used preferably, for example. This ** is preferably used at 0.001 - 10 % of the weight to all volume. In addition, an anti-oxidant, a weatherproof grant agent, an antistatic agent, a bluing agent, etc. can also be contained as an arbitration component.

[0018] Solid content concentration is adjusted to 2 - 50% of the weight, and the above-mentioned solvent solution is used preferably. Spreading can be performed with a dip method, a Floe process, the spinner method, and a spray method.

[0019] As for spreading, it is desirable to carry out by thickness from which the thickness after hardening is set to 1-10 micrometers. If smaller than 1 micrometer, neither xanthochroism-proof nor weatherability is enough, and on the other hand, if larger than 10 micrometers, after giving the rebound ace court back, it becomes easy for a degree of hardness to fall. A solution paint film gives a primer layer after spreading by being heat-treated at the temperature of 100-120 degrees C for 15 minutes to several hours.

[0020] As for the covering polycarbonate plate of this invention, a silicon rebound ace court layer exists on a primer layer. The effective silicon component in a silicon rebound ace court layer It is here. desirable — a silica and following type R1dR2eSi(OR3)4-d-e — R1 The alkyl group of the carbon atomic numbers 1-4, an alkyl halide radical, the aryl group of the carbon atomic numbers 6-12, or an aryl halide radical, The meta-chestnut ROKISHI alkyl group of the carbon atomic numbers 5-8, the ureido alkylene group of the carbon atomic numbers 2-10, They are an aromatic series ureido alkylene group, a halogenated-aromatics alkylene group, or a mercapto alkylene group. R2 The alkyl group of the carbon atomic numbers 1-6, an aryl group, an alkenyl radical, it is an alkyl halide radical or an aryl halide radical, and R3 is a hydrogen atom or the alkyl group of the carbon atomic numbers 1-4, an acyl group, or an alkyl acyl group, and d is 1, 2, or 3, it comes out and e consists of a compound which is 0, 1, or 2 and which is expressed.

[0021] A silica can originate in the multiple oxide particle containing SiO2 in the colloidal silica (sol) which makes an active principle

10 – 50% of the weight of SiO₂, or the range of 1–100nm particle size.

[0022] A multiple oxide is a composite of SiO₂ and a metallic oxide, and can mention the oxide of one sort or two kinds or more of metals chosen from the group which consists of aluminum, Sn, Sb, Ta, Ce, La, Fe, Zn, W, Zr, In, and Ti as this metallic oxide; for example. As an example of a metallic oxide, aluminum 2O₃, SnO₂ and Sb 2O₅, Ta₂O₅, CeO₂ and La 2O₃, Fe₂O₃, ZnO, WO₃, ZrO₂ and In 2O₃, and TiO₂ can be mentioned.

[0023] In order that said multiple oxide may raise the dispersibility to a solvent, surface treatment of it may be carried out with an organic silane compound. The amount of the organic silane compound used is 20 or less % of the weight preferably to multiple oxide particle weight. While the organic silane compound used for processing had had a hydrolysis radical, even if it carries out, surface treatment may be performed after hydrolyzing.

[0024] It is 3 SiX here, as this organic silane compound — the following formula R — It is here, the monofunctional nature silane which are the organic radical on which R has an alkyl group, a phenyl group, a vinyl group, a meta-chestnut ROKISHI radical, a sulphydryl group, an amino group, or an epoxy group, and the radical which can hydrolyze X and which is come out of and expressed, and following formula R₂SiX₂ — It is here, the bifunctional silane as the above with the same definition of R and X come out of and expressed, and the following formula RSiX₃ — the trifunctional silane and the following formula SiX₄ as the above with the same definition of R and X which are come out of and expressed — the definition of X can mention the same tetrafunctional silane as the above come out of and expressed here.

[0025] As a monofunctional nature silane of the above-mentioned formula, for example Trimethylmethoxysilane, Triethylmethoxysilane, trimethylethoxysilane, triethylethoxysilane, Triphenylmethoxysilane, diphenylmethoxysilane, phenyldimethylmethoxysilane, Phenyldimethylethoxysilane, vinyldimethylmethoxysilane, A vinyl dimethylethoxy silane, gamma-acryloxypropyl dimethyl methoxysilane, gamma-methacryloxypropyl dimethyl methoxysilane, gamma-mercapto propyl dimethyl methoxysilane, gamma-mercapto propyl dimethylethoxy silane, N-beta(aminoethyl) gamma-aminopropyl dimethyl methoxysilane, gamma-aminopropyl dimethyl methoxysilane, gamma-aminopropyl dimethylethoxy silane, gamma-glycidoxy propyl dimethyl methoxysilane, gamma-glycidoxy PUROPIRUJI methoxyethoxy silane, and beta-(3,4-epoxycyclohexyl) ethyldimethylmethoxysilane can be mentioned.

[0026] As a bifunctional silane, for example Moreover, dimethyldimethoxysilane, Diethyldimethoxysilane, dimethyl diethoxysilane, diethyldiethoxysilane, Diphenyldimethoxysilane, phenylmethyldimethoxysilane, phenylmethyldiethoxysilane, Vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, gamma-acryloxypropylmethyldimethoxysilane, gamma-methacryloxypropyl dimethyldimethoxysilane, gamma-mercaptpropylmethyl dimethoxysilane, gamma-mercapto propylmethyl diethoxysilane, N-beta (aminoethyl) gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyldiethoxysilane, gamma-glycidoxy propyl methyldimethoxysilane, gamma-glycidoxy propyl methoxy diethoxysilane, and beta-(3,4-epoxycyclohexyl) ethyl methyl dimethoxysilane can be mentioned.

[0027] As a trifunctional silane, for example Moreover, methyl trimetoxysilane, Ethyltrimethoxysilane, methyl triethoxysilane, ethyltriethoxysilane, Phenyltrimethoxysilane, phenyltriethoxysilane, vinyltrimetoxysilane, Vinyltriethoxysilane, a vinyl (beta-methoxyethoxy) silane, gamma-acryloxypropyltrimethoxysilane, gamma-methacryloxypropyl trimethoxy silane, gamma-mercapto propyltrimethoxysilane, gamma-mercapto propyl triethoxysilane, N-beta (aminoethyl) gamma-aminopropyl trimethoxysilane, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-glycidoxypropyltrimetoxysilane, beta-glycidoxy propyltrimethoxysilane, gamma-glycidoxy propyltriethoxysilane, beta-glycidoxy propyltriethoxysilane, and beta-(3,4-epoxycyclohexyl) ethyltrimethoxysilane can be mentioned.

[0028] Furthermore, as a tetrafunctional silane, tetraethyl orthochromatic silicate and tetramethyl alt.silicate can be mentioned, for example. In case a multiple oxide is processed with this silane compound, it is desirable to carry out in water, alcohol, or other organic media.

[0029] As alcohol, for example A methanol, ethanol, isopropyl alcohol, The saturation fatty alcohol like n-butanol and 2-butanol; Methyl cellosolve, The cellosolves like ethylcellosolve, propyl cellosolve, and butyl cellosolve; Propylene glycol monomethyl ether, The propylene glycol monoethyl ether and the propylene glycol derivatives like propylene glycol monomethyl acetate; Methyl acetate, Ether like ethyl acetate, ester; diethylether like butyl acetate, and the methyl isobutyl ether; An acetone, The ketones like methyl isobutyl ketone; a xylene, the aromatic hydrocarbon; ethylene glycol like toluene, a tetrahydrofuran, N and N, - dimethylformamide, a dichloroethane, etc. can be mentioned.

[0030] Another effective silicon component of a silicon rebound ace court layer is a compound expressed with the above-mentioned formula.

[0031] As this compound, for example Trimethylmethoxysilane, triethylmethoxysilane, Trimethylethoxysilane, triethylethoxysilane, triphenylmethoxysilane, Diphenylmethoxysilane, phenyldimethylmethoxysilane, Phenyldimethylethoxysilane, vinyldimethylmethoxysilane, A vinyl dimethylethoxy silane, gamma-acryloxypropyl dimethyl methoxysilane, gamma-methacryloxypropyl dimethyl methoxysilane, gamma-mercapto propyl dimethyl methoxysilane, gamma-mercapto propyl dimethylethoxy silane, N-beta(aminoethyl) gamma-aminopropyl dimethyl methoxysilane, gamma-aminopropyl dimethyl methoxysilane, gamma-aminopropyl dimethylethoxy silane, gamma-glycidoxy propyl dimethyl methoxysilane, gamma-glycidoxy PUROPIRUJI methoxyethoxy silane, beta-(3,4-epoxycyclohexyl) ethyldimethylmethoxysilane dimethyldimethoxysilane, Diethyldimethoxysilane, dimethyl diethoxysilane, diethyldiethoxysilane, Diphenyldimethoxysilane, phenylmethyldimethoxysilane, phenylmethyldiethoxysilane, Vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, gamma-acryloxypropylmethyldimethoxysilane, gamma-methacryloxypropyl dimethyldimethoxysilane, gamma-mercaptpropylmethyl dimethoxysilane, gamma-mercapto propylmethyl diethoxysilane, N-beta (aminoethyl) gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyldiethoxysilane, gamma-glycidoxy propyl methyldimethoxysilane, gamma-glycidoxy propyl methoxy diethoxysilane, beta-(3,4-epoxycyclohexyl) ethyl methyl dimethoxysilane, Methyl trimetoxysilane, ethyltrimethoxysilane, methyl triethoxysilane, Ethyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, Vinyltrimetoxysilane, vinyltriethoxysilane, a vinyl (beta-methoxyethoxy) silane, gamma-acryloxypropyltrimethoxysilane, gamma-methacryloxypropyl trimethoxy silane, gamma-mercapto propyltrimethoxysilane, gamma-mercapto propyl triethoxysilane, N-beta (aminoethyl) gamma-aminopropyl trimethoxysilane, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-glycidoxypropyltrimetoxysilane, beta-glycidoxy propyltrimethoxysilane, gamma-glycidoxy propyltriethoxysilane, beta-glycidoxy propyltriethoxysilane, beta-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, tetraethyl orthochromatic silicate, and tetramethyl orthochromatic silicate can be mentioned.

[0032] As dispersion liquid in a liquid medium which contain the effective silicon component like the above by the specified quantity, a silicon rebound ace court layer is applied on a primer layer, and a liquid medium is removed and it is formed by carrying out heat

hardening.

[0033] As a liquid medium, for example Ethylene glycol monomethyl ether acetate, Ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, Ethylene-glycol-monobutyl-ether acetate, propylene-glycol-monomethyl-ether acetate, Propylene glycol monoethyl ether acetate, propylene glycol monopropylether acetate, Propylene glycol monobutyl ether acetate, ethylene glycol wood ether, Ethylene glycol diethylether, ethylene glycol dipropyl ether, Ethylene glycol dibutyl ether, diethylene-glycol wood ether, Diethylene-glycol diethylether, diethylene-glycol dipropyl ether, Diethylene-glycol dibutyl ether, propylene glycol wood ether, Propylene glycol diethylether, propylene glycol monomethyl ether, The glycols like ethylene glycol monoethyl ether and ethylene glycol monobutyl ether; A cyclohexanone, The aliphatic series annular ketones like o-methylcyclohexanone, m-methylcyclohexanone, and p-methylcyclohexanone; Ethyl-acetate n-propyl acetate, The acetic ester like n-butyl acetate; the alcohols like a methanol, ethanol, 1-propanol, and 2-propanol can be mentioned.

[0034] In the above-mentioned dispersion liquid, the curing catalyst of a rebound ace court layer usually contains. As a curing catalyst, the alkali-metal salt of a carboxylic acid and ammonium salt, the metal salt of an acetylacetone and ammonium salt, the metal salt of ethyl acetoacetate and an acetylacetone and the metal salt which ethyl acetoacetate configured, the 1st - tertiary amine, a polyalkylene amine, sulfonate, magnesium perchlorate, an ammonium perchlorate, etc. can be mentioned, for example. These compounds can also be used together with an organic mercaptan or a mercapto alkylene silane.

[0035] As an example of the above-mentioned metal salt, salts with the chelate compound or aliphatic series acid containing the following core metal can be mentioned. The central metal like aluminum, Zr, Co, Zn, Sn, Mn, V, Cu, Ce, Cr, Ru, Ga, Cd, and Fe; An acetylacetone, G n-butoxide-monochrome-ethyl Acetate, G n-butoxide-monochrome-methyl Chelate compound; like acetate, methylethyl ketoxime, 2, 4-hexane dione, 3, 5-heptane dione, and the aceto oxime And the aliphatic series acid compound like a 2-ethyl-hexyl acid, stearin acid, a lauric acid, oleic acid, an acetic acid, a sebacic acid, dodecane diacid, a propionic acid, a brasylic acid, an isobutyl acid, and a citraconic acid.

[0036] As an example of the 1st - the 3rd amine, moreover, fatty amine, aromatic amine, An amino silane etc. is desirable. For example, polymethylene diamine, polyether diamine, Diethylenetriamine, iminobis propylamine, bis-hexamethylene triamine, Diethylenetriamine, a tetra-ethylene PENTA amine, a pentaethylene hexa amine, Pentaethylenhexamine, dimethylamino propylamine, aminoethylethanolamine, Methyliminobispropylamine, menthonaphtene diamine, N-friend NOMECHI ruby perazine, 1, 3-diamino cyclohexane, isophorone diamine, meta-xylene diamine, Tetra-chloro paraxylene diamine, meta-phenylenediamine, 4, and 4'-methylenedianiline, Diamino diphenyl sulfone, a benzidine, a toluidine, diamino diphenyl ether, - thio dianiline, and 4 and 4' 4, 4'-screw (ortho toluidine) dianisidine, o-phenylenediamine, 2, 4-toluene diamine, methylenebis (o-chloroaniline), JIAMINJI tolyl sulfone, screw (3, 4-diamino phenyl) sulfone, 2, 6-diamino pyridine, a 4-chloro-o-phenylenediamine, A 4-methoxy-6-methyl-m-phenylenediamine, m-amino benzylamine, N, N, N', N'- tetramethyl-1, 3-butanediamine, N and N, N', N'-tetramethyl-p-phenylene diamine, Tetramethyl guanidine, triethanolamine, a 2-dimethylamino-2-hydroxy propane, N, - dimethyl piperazine, and N'N, N' screw [-] [(2-hydroxy) propyl] piperazine, N-methyl HORUMORIN, a hexamethylenetetramine, a pyridine, pyrazine, A quinoline, benzyl dimethylamine, alpha-methylbenzyl monomethylamine, 2-(dimethyl aminomethyl) phenol, 2 and 4, 6-tris (dimethylamino methylol) phenol, N-methyl piperazine, a pyrrolidine, HORUMORIN, N-beta (aminoethyl) gamma-aminopropyl trimethoxysilane, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, N-beta(aminoethyl) gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, and gamma-aminopropyl methyl diethoxysilane can be mentioned.

[0037] The curing catalyst like the above can be added also in the time of preparation of dispersion liquid just before spreading. The rate of a curing catalyst is 0.001 - 10 % of the weight preferably to the effective formed element in dispersion liquid.

[0038] In order to avoid the operation which the excessive activity energy which the photocatalyst coat which mentions the above-mentioned dispersion liquid for a silicon rebound ace court layer later in this invention has spreads, and promotes degradation of resin, it is desirable to contain the compound which has the operation which eases this activity energy.

[0039] As this compound, the metal chelate compound whose structure of a chelate is aliphatic series, for example, and the compound of an aliphatic series acid metal salt are desirable, and what has compatibility in the matrix resin of a rebound ace court layer is still more desirable.

[0040] As a central metal of this compound, Co, Mn, V, Cu, Ce, Cr, Ru, Ga, Cd, and Fe can be mentioned, for example. Moreover, as a chelate compound, they are an acetylacetone and G n-butoxide-monochrome-ethyl, for example. Acetate, G n-butoxide-monochrome-methyl Acetate, methylethyl ketoxime, 2, 4-hexane dione, 3, and 5-heptane dione and the aceto oxime can be mentioned. Furthermore, as an aliphatic series acid compound, a 2-ethyl-hexyl acid, stearin acid, a lauric acid, oleic acid, an acetic acid, a sebacic acid, dodecane diacid, a propionic acid, a brasylic acid, an isobutyl acid, and a citraconic acid can be mentioned, for example. That to which the solution containing it presents a purplish red color from blue with an absorption peak is desirable to 400-550nm of these compounds.

[0041] This compound is preferably used at 0.001 - 5 % of the weight to the solid content in dispersion liquid. The effectiveness which used this compound when fewer than 0.001 % of the weight is hardly acquired, but when [than 5 % of the weight] more [again], the degree of hardness of a rebound ace court layer tends to deteriorate.

[0042] Moreover, the above-mentioned dispersion liquid can contain the leveling agent of a hardening coat, and a lubricative grant agent as an arbitration component. As this **, the copolymer of polyoxyalkylene, the copolymer (paint additive 31 of Dow Corning) of poly dimethylsiloxane and polyoxyalkylene, and fluorocarbon is used preferably, for example. This ** is preferably used at 0.001 - 10 % of the weight to all volume. In addition, an anti-oxidant, a weatherproof grant agent, an antistatic agent, a bluing agent, etc. can also be contained as an arbitration component.

[0043] Solid content concentration is adjusted to 2 - 50% of the weight, and the above-mentioned dispersion liquid are used preferably. Spreading can be performed with a dip method, a Floe process, the spinner method, and a spray method.

[0044] As for spreading, it is desirable to carry out by thickness from which the thickness after hardening is set to 2-7 micrometers. If smaller than 2 micrometers, a degree of hardness is not enough, and on the other hand, if larger than 7 micrometers, it will become easy to generate a crack in a rebound ace court layer. A dispersion-liquid paint film gives a silicon rebound ace court layer after spreading by being heat-treated at the temperature of 100-130 degrees C for 1 to 24 hours.

[0045] The covering polycarbonate plate of this invention has a photocatalyst coat further on a silicon rebound ace court layer. This layer consists of silicon resin containing the metallic oxide which has the photocatalyst effectiveness. The metallic-oxide particle which generates the band gap which discovers the photocatalyst effectiveness by UV irradiation as a metallic oxide which has the photocatalyst effectiveness is desirable. As this particle, TiO₂, TiO₃, SrTiO₃, FeTiO₃, WO₃, SnO₂, Bi₂O₃, In₂O₃, ZnO and Fe₂O₃, RuO₂, CdO and CdS, CdSe, GaP, GaAs, CdFeO₃ and MoS₂, and LaRhO₃ grade can be mentioned, for example. It is TiO₂ and ZnO preferably and is the anatase mold TiO₂ especially preferably.

[0046] moreover, following type: $R_1dR_2eSi(OR_3)_4-d-e$ which indicated the silicon rebound ace court layer as silicon resin — it is here and the definition of R_1 , R_2 , R_3 , d , and e can mention the hardened material of the same compound as the above come out of and expressed as a desirable thing.

[0047] The same thing as what indicated the rebound ace court etc. also as a curing catalyst and a liquid medium can be used. As a liquid medium, 1-propanol is desirable especially here. As for the coating liquid for a photocatalyst coat, it is desirable that solid content concentration is 1 – 10 % of the weight.

[0048] Spreading can be performed with a dip method, a Floe process, the spinner method, and a spray method. As for spreading, it is desirable to carry out by thickness from which the thickness after hardening is set to 5–50nm. If larger than 50nm, the film will become cloudy, and the interference color is not visible and desirable. A solution paint film gives a photocatalyst coat after spreading by being heat-treated at the temperature of 100–130 degrees C for 1 to 5 hours.

[0049] As for a photocatalyst coat, it is desirable to prepare on the silicon rebound ace court layer which carried out corona treatment. A photocatalyst coat is joined still more strongly in a silicon rebound ace court layer by it. Moreover, a photocatalyst coat can be made to contain the compound which has the operation which eases this activity energy in order to avoid the operation which the excessive activity energy which the compound, i.e., a photocatalyst layer, which indicated the rebound ace court layer has spreads, and promotes degradation of resin.

[0050] The covering polycarbonate plate of this invention can be used for a sound-proof wall, a grading application, and an inside-of-a-house application.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, this invention is further explained in full detail according to an example. The various matter used in the example is as follows.

Polycarbonate plate: The plate (1mx30cmx5mm) with a PORIKA ace (product made from Plastics In cylinder) thickness of 5mm was used.

[0053] Primer 1: They are 850g and Dow in the copolymer ($M_n=10000$, $M_w=40000$) of 4:1 at the mole ratio of methyl methacrylate and methacryloxy propyl trimethoxysilane aboutg [100], 2, and 4-dihydroxy benzophenone 50g and propylene glycol monomethyl ether. Solution which consists the Corning paint additive 31 of 0.1g.

[0054] primer 2: — acryloid A-10S (acrylic resin by loam & Haas) — 100g, 2, 2', 4, and 4' - tetra-hydroxy benzophenone 40g and propylene glycol monomethyl ether — 860g and Dow Solution which consists the Corning paint additive 31 of 0.1g.

[0055] Rebound ace court 1: Snow tex 0-40 (the product made from the Nissan chemistry: colloidal silica, moisture powder, 40% of nonvolatile matters) Isopropyl alcohol 648g, 2g of sodium acetate, Dow after making 150g and methyl trimetoxysilane 200g react Solution which added 0.1g for the Corning paint additive 31.

[0056] Rebound ace court 2: Snow tex 0-40 (the product made from the Nissan chemistry: colloidal silica, moisture powder, 40% of nonvolatile matters) 2 and 4-dihydroxy benzophenone 20g, isopropyl alcohol 628g, 2g of sodium acetate, Dow after making 150g and methyl trimetoxysilane 200g react Solution which consists the Corning paint additive 31 of 0.1g.

[0057] Rebound ace court 3: Snow tex 0-40 (the product made from the Nissan chemistry: colloidal silica, moisture powder, 40% of nonvolatile matters) They are 0.1g, 2g of sodium acetate, and Dow about isopropyl alcohol after making 150g and methyl trimetoxysilane 200g react 647g, and Co(II) acetylacetone 2 hydrate. Solution which added 0.1g of Corning paint additives 31.

[0058] The solution containing TiO₂: The solution which consists ST-K03 (the Ishihara Sangyo make, 10% of nonvolatile matters) of 50wt(s)% and 1-propyl alcohol 50wt%.

[0059] Moreover, the conditions and the various examining methods which were used in the example, such as the method of application, are as follows.

[0060] Method of application: A flow coat or a DIP coat.

Corona-treatment conditions: Output 500W, the irradiation range of 5mm, processing during 3 minutes.

Rebound-ace-court hardening conditions: It is 60 minutes at 120 degrees C.

The hardening conditions of the solution containing TiO₂: It is 120 degrees C and is 30 to 60 minutes.

[0061] Adhesion: Go board trial JIS It is based on K5400.

Whenever [yellow]: JIS It measures according to K7103.

Hardness: JIS It is too heavy 500g at the Taber abrasion test based on K7204, and the turbidity before and behind 500 rotations is measured.

Turbidity: JIS It is based on K7105.

An early contact angle: Measure a contact angle with 0.1 cc waterdrop after irradiating the light source of 2 the ultraviolet-rays reinforcement of 0.5mW/cm for 3 hours.

The contact angle after a weathering test: Measure a contact angle with 0.1 cc waterdrop.

[0062] Weatherability 1: Evaluate the appearance of 3000 hours after, and adhesion using a sunshine carbon arc weatherometer weatherability accelerated test machine (the black panel temperature of 63 degrees C and a water spray are sprayed for 12 minutes per hour).

[0063] The primer 1 was carried out in the flow coat, spreading hardening of the rebound ace court 1 was carried out in the flow coat at the example 1 polycarbonate plate after spreading hardening (1.8-3.5 micrometers in thickness of the primer layer after hardening) (2-5 micrometers in thickness of the rebound ace court layer after hardening), spreading hardening of the solution which contains the corona treatment back TiO₂ further was carried out, and thickness of the photocatalyst coat after hardening was set to 20-40nm.

[0064] Example 2 primer 2 was carried out in the flow coat, spreading hardening of the rebound ace court 2 was carried out in the flow coat after spreading hardening (1-2 micrometers in thickness after hardening) (2-5.5 micrometers of thickness of the rebound ace court layer after hardening), spreading hardening of the solution containing the corona treatment back TiO₂ was carried out, and thickness of the photocatalyst coat after hardening was set to 20-40nm.

[0065] Example 3 primer 1 is applied on a DIP coat (a part for 1.5m/in raising rate). At 115 degrees C, after hardening during 30 minutes (1.8-3.5 micrometers in thickness of the primer layer after hardening). The rebound ace court 3 was applied on the DIP coat (a part for 1.5m/in raising rate), it hardened for 60 minutes at 120 degrees C (thickness of 2-5 micrometers of the rebound ace court layer after hardening), spreading strengthening of the solution containing the corona treatment back TiO₂ was carried out, and thickness of the photocatalyst coat after hardening was set to 20-40nm.

[0066] The process after corona treatment was not carried out in example of comparison 1 example 1, but others were performed similarly to an example 1.

[0067] In example of comparison 2 example 1, the process which carries out spreading hardening of the rebound ace court 1 was not carried out, but others were performed similarly to an example 1. The result was shown in Table 1 and 2.

[0068]

[Table 1]

項目	初期性能				
	密着性	硬度	ヘイズ率	YI	初期接触角
実施例1	100%	2%	0.5%	-1.0	1°
実施例2	100%	4%	0.6%	0.1	1°
実施例3	100%	2%	0.6%	-1.5	1°
比較例1	100%	2%	0.2%	-1.0	85°
比較例2	100%	20%	0.4%	0.8	2°

[0069]

[Table 2]

項目	耐候性試験後				
	密着性	硬度	ヘイズ率	YI	接触角
実施例1	100%	4%	1%	1.0	6°
実施例2	100%	8%	2%	2.0	8°
実施例3	100%	4%	1%	0.5	3°
比較例1	100%	5%	1%	1.5	72°
比較例2	0%	20%	10%	18%	55°

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(54) 【発明の名称】 被覆ポリカーボネート板

(57) 【要約】

【課題】 長期間にわたり屋外で使用しても黄変がなく、曇りもない表面防曇性、防汚性を有した透明ハードコート付きポリカーボネート板を提供すること。

【解決手段】 ポリカーボネート板上に、有効不揮発分の20重量%以上の紫外線吸収剤を含む有機樹脂からなるプライマー層、シリコンハードコート層および光触媒効果を有する金属酸化物を含むシリコン樹脂からなる光触媒塗膜層がこの順番で積層されてなる被覆ポリカーボネート板。

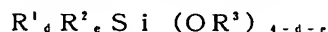
【特許請求の範囲】

【請求項1】 ポリカーボネート板上に、有効不揮発分の20重量%以上の紫外線吸収剤と有機樹脂からなるプライマー層、シリコンハードコート層および光触媒効果を有する金属酸化物を含むシリコン樹脂からなる光触媒塗膜層がこの順番で積層されてなる被覆ポリカーボネート板。

【請求項2】 プライマー層中の紫外線吸収剤がベンゾフェノン系である請求項1に記載の被覆ポリカーボネート板。

【請求項3】 プライマー層中の有機樹脂がアクリルポリマーまたはアクリルモノマーとメタクリロキシシランの共重合体である請求項1に記載の被覆ポリカーボネート板。

【請求項4】 シリコンハードコート層中の有効シリコン成分がシリカと下記式



ここで、 R^1 は炭素原子数1~4のアルキル基、ハロゲン化アルキル基、炭素原子数6~12のアリール基またはハロゲン化アリール基、炭素原子数5~8のメタクリロキシアリール基、炭素原子数2~10のウレイドアルキレン基、芳香族ウレイドアルキレン基、ハロゲン化芳香族アルキレン基またはメルカプトアルキレン基であり、 R^2 は炭素原子数1~6のアルキル基、アリール基、アルケニル基、ハロゲン化アルキル基またはハロゲン化アリール基であり、 R^3 は水素原子もしくは炭素原子数1~4のアルキル基、アシル基またはアルキルアシル基であり、そしてdは1、2または3であり、eは0、1または2である、で表される化合物からなる請求項1に記載の被覆ポリカーボネート板。

【請求項5】 シリコンハードコート層が光触媒塗膜層の持つ余分な活性エネルギーが伝播して樹脂の劣化を促進する作用を回避する為に、該活性エネルギーを緩和する作用を有する化合物を含有する請求項1に記載の被覆ポリカーボネート板。

【請求項6】 活性エネルギーを緩和する作用を有する化合物がキレート構造が脂肪族である金属キレート化合物または脂肪族酸の金属塩でありそしてハードコートのマトリックス樹脂に相溶性を持つ請求項5に記載の被覆ポリカーボネート板。

【請求項7】 活性エネルギーを緩和する作用を有する化合物が400~550nmに吸収ピークを持ちそしてそれを含有溶液が青から赤紫色を呈する請求項5に記載の被覆ポリカーボネート板。

【請求項8】 光触媒塗膜層がコロナ処理されたシリコンハードコート層上に設けられる請求項1に記載の被覆ポリカーボネート板。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は被覆ポリカーボネ

ート板に関する。さらに詳しくは屋外使用時にも防曇性を持続し且つ黄変のないポリカーボネート板に関する。

【0002】

【従来の技術】 特開平2-274736号公報には、

(a) アルコキシシリル基を持つ(メタ)アクリル単量体とアルキル(メタ)アクリレートとの共重合体、

(b) 過塩素酸アンモニウムおよび(c) 紫外線吸収剤を含む組成物の硬化した下塗り層並びにコロイダルシリカ含有オルガノポリシロキサン含有組成物の硬化した上塗り層からなる、耐摩耗性と耐候性の改善された被覆ポリカーボネート物品が開示されている。

【0003】 特開平10-245521号公報には、ポリカーボネートの如き有機樹脂基材に塗布するケイ素コーティング剤用のプライマー組成物として、(メタ)アクリル系樹脂および/またはビニル系樹脂であるバインダー樹脂およびこのバインダー樹脂に対し0.1~30重量%の、320~400nmの紫外線を吸収する無機化合物の配合物が開示されている。

【0004】 特開平11-58654号公報には、ポリカーボネート板の少なくとも一面にプライマー塗料を塗布、硬化させ、次いでその上にトップ塗料を塗布、硬化させて得られた耐候性に優れたポリカーボネート樹脂積層板が開示されている。上記プライマー塗料は2,2',4,4'-テトラヒドロベンゾフェノンを含むベンゾフェノン系紫外線吸収剤を塗料の不揮発分100重量部当たり8~17重量部含む熱硬化性アクリル樹脂からなり、またトップ塗料は上記紫外線吸収剤を塗料の不揮発分100重量部当たり1~4重量部含むコロイダルシリカ含有ポリオルガノシロキサンからなる。

【0005】 さらに、特開平10-195829号公報には、ポリカーボネートの如き基材の表面に、アナターゼ型酸化チタンの如き光触媒の粒子と、撥水性シリコンと、この撥水性シリコンの前記光触媒の光励起による親水化を防止するための物質例えばコバルト化合物とを、含有する表面層を持つ遮音壁が開示されている。

【0006】 特開平10-67873号公報には、アクリル樹脂の如き樹脂の表面を親水化処理し、処理された表面を光触媒とシリコン樹脂を含む層で被覆しそして該シリコン樹脂のケイ素原子に結合する有機基の少なくとも1部を水酸基に置換することからなる樹脂基材表面の親水化法が開示されている。

【0007】 最後に、特開平11-61044号公報には、ポリオルガノシロキサンと、光触媒機能を有する無機粒子を含有する塗膜を表面に有する建材が開発されている。

【0008】 上記の如き、従来技術の構成では、光触媒の作用によりマトリックス樹脂であるシリコン樹脂およびプライマー樹脂の劣化が起こり、その結果クラックが発生したり、剥離したりして光触媒塗膜を保持できず、紫外線により樹脂基材が劣化し、屋外で使用する場合十

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分な耐候性を発現できるものが知られていなかった。

【0009】

【発明が解決しようとする課題】本発明の目的は、新規な構成の被覆層を備えた、被覆ポリカーボネート板を提供することにある。本発明の他の目的は、長期間に亘り屋外で使用しても防曇性を持続することができしかも黄変や曇りのない被覆ポリカーボネート板を提供することにある。本発明のさらに他の目的および利点は、以下の説明から明らかになる。

【0010】

【課題を解決するための手段】本発明によれば、本発明の上記目的および利点は、ポリカーボネート板上に、有効不揮発分の20重量%以上の紫外線吸収剤を含む有機樹脂からなるプライマー層、シリコンハードコート層および光触媒効果を有する金属酸化物を含むシリコン樹脂からなる光触媒塗膜層がこの順番で積層されてなる被覆ポリカーボネート板によって達成される。

【0011】プライマー層は有効不揮発分の20重量%以上の紫外線吸収剤と有機樹脂からなる。有機樹脂としては、ポリカーボネート板に密着し且つシリコンハードコートと接着可能な樹脂が用いられる。かかる有機樹脂は公知であり、例えばアクリルポリマー、アクリルモノマーとメタクリロキシシランとの共重合体、あるいはベンゾトリアゾール基やベンゾフェノン基を持つメタクリルモノマーとアクリルモノマーとの共重合体を好ましいものとして挙げることができる。これらのうち、アクリルポリマーおよびアクリルモノマーをメタクリロキシシランとの共重合体がさらに好ましい。有機樹脂は1種でまたは2種以上一緒に用いることができる。

【0012】また、プライマー層が含有する紫外線吸収剤としては、例えばベンゾトリアゾール系およびベンゾフェノン系を好ましいものとして挙げることができる。これらのうち、ベンゾフェノン系がさらに好ましい。紫外線吸収剤は1種でまたは2種以上一緒にして用いることができる。

【0013】ベンゾトリアゾール系紫外線吸収剤としては、例えば2-(2'-ヒドロキシ-5'-メチルフェニル)-ベンゾトリアゾール、2-(2'-ヒドロキシ-3',5'-ジ-*t*-ブチルフェニル)-ベンゾトリアゾール、2-(2'-ヒドロキシ-5'-*t*-ブチルフェニル)-ベンゾトリアゾール、2-(2'-ヒドロキシ-5'-*t*-オクチルフェニル)-ベンゾトリアゾール、2-(2'-ヒドロキシ-3',5'-ジ-*t*-ブチルフェニル)-5-クロロベンゾトリアゾール、あるいはチバ・スペシャルティ・ケミカルズ株式会社のチヌビン328、チヌビン384、チヌビン900、チヌビン928、チヌビン1130を挙げることができる。

【0014】ベンゾフェノン系紫外線吸収剤としては、例えば2,4-ジヒドロキシベンゾフェノン、2-ヒド

ロキシ-4-メトキシベンゾフェノン、2,2'-ヒドロキシ-4-メトキシベンゾフェノン、2,2',4,4'-テトラヒドロキシベンゾフェノン、2,2'-ジヒドロキシ-4,4'-ジメトキシベンゾフェノンを挙げることができる。また、紫外線吸収剤としては、この他ベンゾトリアゾールまたはベンゾフェノン基を有するシラン化合物を用いることもできる。

【0015】かかる紫外線吸収剤はプライマー層中の有効不揮発成分の20重量%以上、好ましくは20~60重量%、さらに好ましくは20~50重量%で含有される。プライマー層は、紫外線吸収剤および有機樹脂を所定量で含む溶媒溶液を、ポリカーボネート基板上に塗布し、溶媒を除去し、加熱硬化せしめることにより形成される。

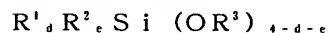
【0016】溶媒としては、例えばエチレングリコールモノメチルエーテルアセテート、エチレングリコールモノエチルエーテルアセテート、エチレングリコールモノプロピルエーテルアセテート、エチレングリコールモノブチルエーテルアセテート、プロピレングリコールモノメチルエーテルアセテート、プロピレングリコールモノエチルエーテルアセテート、プロピレングリコールモノプロピルエーテルアセテート、プロピレングリコールモノブチルエーテルアセテート、エチレングリコールジメチルエーテル、エチレングリコールジエチルエーテル、エチレングリコールジプロピルエーテル、エチレングリコールジブチルエーテル、ジエチレングリコールジメチルエーテル、ジエチレングリコールジエチルエーテル、ジエチレングリコールジプロピルエーテル、ジエチレングリコールジブチルエーテル、プロピレングリコールジメチルエーテル、プロピレングリコールジエチルエーテル、プロピレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、エチレングリコールモノブチルエーテルの如きグリコール類；シクロヘキサノン、*o*-メチルシクロヘキサノン、*m*-メチルシクロヘキサノン、*p*-メチルシクロヘキサノンの如き脂肪族環状ケトン類；酢酸エチル酢酸*n*-プロピル、酢酸*n*-ブチルの如き酢酸エステル類；メタノール、エタノール、1-プロパノール、2-プロパノールの如きアルコール類およびソルベントナフサ、メチルエチルケトン等を挙げることができる。

【0017】また、上記溶媒溶液は、任意成分として、硬化被膜のレベリング剤、潤滑性付与剤を含有することができる。かかる剤としては、例えばポリオキシアルキレンとポリジメチルシロキサンとの共重合体（ダウコーニング社のペイントアディティブ31）、ポリオキシアルキレンとフルオロカーボンとの共重合体が好ましく用いられる。かかる剤は、全液量に対して0.001~10重量%で好ましく使用される。その他任意成分として酸化防止剤、耐候性付与剤、帯電防止剤、ブルーイング剤等を含有することもできる。

【0018】上記溶媒溶液は、固形分濃度が例えば2～50重量%に調整されて好ましく用いられる。塗布は、例えばディップ法、フロー法、スピンナー法、スプレー法により行うことができる。

【0019】塗布は、硬化後の膜厚が1～10 μ mとなるような厚さで実施するのが好ましい。1 μ mより小さいと耐黄変性や耐候性が十分でなく、一方10 μ mより大きいとハードコート後を施したのち硬度が低下し易くなる。塗布後、溶液塗膜は例えば15分～数時間、100～120℃の温度で加熱処理されることにより、プライマー層を与える。

【0020】本発明の被覆ポリカーボネート板はプライマー層の上にシリコンハードコート層が存在する。シリコンハードコート層中の有効シリコン成分は、好ましくはシリカと下記式



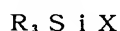
ここで、 R^1 は炭素原子数1～4のアルキル基、ハロゲン化アルキル基、炭素原子数6～12のアリール基またはハロゲン化アリール基、炭素原子数5～8のメタクリロキシアリル基、炭素原子数2～10のウレイドアルキレン基、芳香族ウレイドアルキレン基、ハロゲン化芳香族アルキレン基またはメルカプトアルキレン基であり、 R^2 は炭素原子数1～6のアルキル基、アリール基、アルケニル基、ハロゲン化アルキル基またはハロゲン化アリール基であり、 R^3 は水素原子もしくは炭素原子数1～4のアルキル基、アシル基またはアルキルアシル基であり、そしてdは1、2または3であり、eは0、1または2である、で表される化合物からなる。

【0021】シリカは例えば10～50重量%の SiO_2 を有効成分とするコロイダルシリカ（ゾル）あるいは粒径1～100nmの範囲にある SiO_2 を含む複合酸化物微粒子に由来することができる。

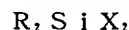
【0022】複合酸化物は SiO_2 と金属酸化物との複合物であり、かかる金属酸化物としては、例えば、Al、Sn、Sb、Ta、Ce、La、Fe、Zn、W、Zr、InおよびTiよりなる群から選ばれる1種もしくは2種類以上の金属の酸化物を挙げることができる。金属酸化物の具体例としては、 Al_2O_3 、 SnO_2 、 Sb_2O_3 、 Ta_2O_5 、 CeO_2 、 La_2O_3 、 Fe_2O_3 、 ZnO 、 WO_3 、 ZrO_2 、 In_2O_3 および TiO_2 を挙げることができる。

【0023】前記複合酸化物は溶媒への分散性を高めるため有機シラン化合物で表面改質してもよい。有機シラン化合物の使用量は、複合酸化物微粒子重量に対して、好ましくは20重量%以下である。表面処理は、処理に用いる有機シラン化合物が加水分解基を持ったままで行っても、加水分解した後で行ってもよい。

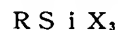
【0024】かかる有機シラン化合物としては、例えば下記式



ここで、Rはアルキル基、フェニル基、ビニル基、メタクリロキシ基、メルカプト基、アミノ基またはエポキシ基を有する有機基、Xは加水分解可能な基である、で表される単官能性シラン、下記式



ここで、RおよびXの定義は上記に同じである、で表される二官能性シラン、下記式



ここで、RおよびXの定義は上記に同じである、で表される三官能性シランおよび下記式



ここでXの定義は上記に同じである、で表される四官能性シランを挙げることができる。

【0025】上記式の単官能性シランとしては、例えばトリメチルメトキシシラン、トリエチルメトキシシラン、トリメチルエトキシシラン、トリエチルエトキシシラン、トリフェニルメトキシシラン、ジフェニルメチルメトキシシラン、フェニルジメチルメトキシシラン、フェニルジメチルエトキシシラン、ビニルジメチルメトキシシラン、ビニルジメチルエトキシシラン、 γ -アクリロキシプロピルジメチルメトキシシラン、 γ -メタクリロキシプロピルジメチルメトキシシラン、 γ -メルカプトプロピルジメチルメトキシシラン、 γ -メルカプトプロピルジメチルエトキシシラン、N- β （アミノエチル） γ -アミノプロピルジメチルメトキシシラン、 γ -アミノプロピルジメチルメトキシシラン、 γ -アミノプロピルジメチルエトキシシラン、 γ -グリシドキシプロピルジメチルメトキシシラン、 γ -グリシドキシプロピルジメトキシエトキシシランおよび β -（3,4-エポキシクロヘキシル）エチルジメチルメトキシシランを挙げることができる。

【0026】また、二官能性シランとしては、例えば、ジメチルジメトキシシラン、ジエチルジメトキシシラン、ジメチルジエトキシシラン、ジエチルジエトキシシラン、ジフェニルジメトキシシラン、フェニルメチルジメトキシシラン、フェニルメチルジエトキシシラン、ビニルメチルジメトキシシラン、ビニルメチルジエトキシシラン、 γ -アクリロキシプロピルメチルジメトキシシラン、 γ -メタクリロキシプロピルメチルジメトキシシラン、 γ -メルカプトプロピルメチルジメトキシシラン、 γ -メルカプトプロピルメチルジエトキシシラン、N- β （アミノエチル） γ -アミノプロピルメチルジメトキシシラン、 γ -アミノプロピルメチルジメトキシシラン、 γ -アミノプロピルメチルジエトキシシラン、 γ -グリシドキシプロピルメチルジメトキシシラン、 γ -グリシドキシプロピルメトキシジエトキシシランおよび β -（3,4-エポキシクロヘキシル）エチルメチルジメトキシシランを挙げることができる。

【0027】また、三官能性シランとしては、例えば、メチルトリメトキシシラン、エチルトリメトキシシラ

ン、メチルトリエトキシシラン、エチルトリエトキシシラン、フェニルトリエトキシシラン、フェニルトリエトキシシラン、ビニルトリエトキシシラン、ビニルトリエトキシシラン、ビニル(β-メトキシエトキシ)シラン、γ-アクリロキシプロピルトリエトキシシラン、γ-メタクリロキシプロピルトリエトキシシラン、γ-メルカプトプロピルトリエトキシシラン、γ-メルカプトプロピルトリエトキシシラン、N-β(アミノエチル)γ-アミノプロピルトリエトキシシラン、γ-アミノプロピルトリエトキシシラン、γ-アミノプロピルトリエトキシシラン、γ-グリシドキシプロピルトリエトキシシラン、β-グリシドキシプロピルトリエトキシシラン、γ-グリシドキシプロピルトリエトキシシラン、β-グリシドキシプロピルトリエトキシシランおよびβ-(3,4-エポキシシクロヘキシル)エチルトリエトキシシランを挙げることができる。

【0028】さらに、四官能性シランとしては、例えば、テトラエチルオルソシリケートおよびテトラメチルオルトシリケートを挙げることができる。複合酸化物をかけるシラン化合物で処理する際には、例えば水、アル

コールあるいはその他の有機媒体中で行うことが好ましい。

【0029】アルコールとしては、例えば、メタノール、エタノール、イソプロピルアルコール、n-ブタノール、2-ブタノールの如き飽和脂肪族アルコール類；メチルセロソルブ、エチルセロソルブ、プロピルセロソルブ、ブチルセロソルブの如きセロソルブ類；プロピレングリコールモノメチルエーテル、プロピレングリコールモノエチルエーテル、プロピレングリコールモノメチルアセテートの如きプロピレングリコール誘導体類；酢酸メチル、酢酸エチル、酢酸ブチルの如きエステル類；ジエチルエーテル、メチルイソブチルエーテルの如きエーテル類；アセトン、メチルイソブチルケトンの如きケトン類；キシレン、トルエンの如き芳香族炭化水素類；エチレングリコール、テトラヒドロフラン、N,N-ジメチルホルムアミド、ジクロロエタン等を挙げることができる。

【0030】シリコンハードコート層のもう一方の有効シリコン成分は上記式で表される化合物である。

【0031】かかる化合物としては、例えば、トリメチルメトキシシラン、トリエチルメトキシシラン、トリメチルエトキシシラン、トリエチルエトキシシラン、トリフェニルメトキシシラン、ジフェニルメチルメトキシシラン、フェニルジメチルメトキシシラン、フェニルジメチルエトキシシラン、ビニルジメチルメトキシシラン、γ-アクリロキシプロピルジメチルメトキシシラン、γ-メタクリロキシプロピルジメチルメトキシシラン、γ-メルカプトプロピルジメチルメトキシシラン、γ-メルカプトプロピルジメチルエトキシシラン、N-β(アミノエチル)γ-アミ

ノプロピルジメチルメトキシシラン、γ-アミノプロピルジメチルメトキシシラン、γ-アミノプロピルジメチルエトキシシラン、γ-グリシドキシプロピルジメチルメトキシシラン、γ-グリシドキシプロピルジメチルエトキシシラン、β-(3,4-エポキシシクロヘキシル)エチルジメチルメトキシシランジメチルジメトキシシラン、ジエチルジメトキシシラン、ジメチルジエトキシシラン、ジエチルジエトキシシラン、ジフェニルジメトキシシラン、フェニルメチルジメトキシシラン、フェニルメチルジエトキシシラン、ビニルメチルジメトキシシラン、ビニルメチルジエトキシシラン、γ-アクリロキシプロピルメチルジメトキシシラン、γ-メタクリロキシプロピルジメチルジメトキシシラン、γ-メルカプトプロピルメチルジエトキシシラン、N-β(アミノエチル)γ-アミノプロピルメチルジメトキシシラン、γ-アミノプロピルメチルジメトキシシラン、γ-アミノプロピルメチルジエトキシシラン、γ-グリシドキシプロピルメチルジメトキシシラン、γ-グリシドキシプロピルメトキシジエトキシシラン、β-(3,4-エポキシシクロヘキシル)エチルメチルジメトキシシラン、メチルトリエトキシシラン、エチルトリエトキシシラン、メチルトリエトキシシラン、エチルトリエトキシシラン、フェニルトリエトキシシラン、フェニルトリエトキシシラン、ビニルトリエトキシシラン、ビニルトリエトキシシラン、ビニル(β-メトキシエトキシ)シラン、γ-アクリロキシプロピルトリエトキシシラン、γ-メタクリロキシプロピルトリエトキシシラン、γ-メルカプトプロピルトリエトキシシラン、γ-メルカプトプロピルトリエトキシシラン、N-β(アミノエチル)γ-アミノプロピルトリエトキシシラン、γ-アミノプロピルトリエトキシシラン、γ-アミノプロピルトリエトキシシラン、γ-グリシドキシプロピルトリエトキシシラン、β-グリシドキシプロピルトリエトキシシラン、γ-グリシドキシプロピルトリエトキシシラン、β-グリシドキシプロピルトリエトキシシラン、β-(3,4-エポキシシクロヘキシル)エチルトリエトキシシラン、テトラエチルオルソシリケート、テトラメチルオルソシリケートを挙げることができる。

【0032】シリコンハードコート層は、上記の如き有効シリコン成分を所定量で含む液体媒体中分散液として、プライマー層上に塗布され、液体媒体を除去されそして加熱硬化されることにより形成される。

【0033】液体媒体としては、例えばエチレングリコールモノメチルエーテルアセテート、エチレングリコールモノエチルエーテルアセテート、エチレングリコールモノブチルエーテルアセテート、プロピレングリコールモノメチルエーテルアセテート、プロピレングリコールモノエチルエーテルアセテート、プロピレングリコール

モノプロピルエーテルアセテート、プロピレングリコールモノブチルエーテルアセテート、エチレングリコールジメチルエーテル、エチレングリコールジエチルエーテル、エチレングリコールジプロピルエーテル、エチレングリコールジブチルエーテル、ジエチレングリコールジメチルエーテル、ジエチレングリコールジエチルエーテル、ジエチレングリコールジプロピルエーテル、ジエチレングリコールジブチルエーテル、プロピレングリコールジメチルエーテル、プロピレングリコールジエチルエーテル、プロピレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテルおよびエチレングリコールモノブチルエーテルの如きグリコール類；シクロヘキサノン、*o*-メチルシクロヘキサノン、*m*-メチルシクロヘキサノン、*p*-メチルシクロヘキサノンの如き脂肪族環状ケトン類；酢酸エチル酢酸*n*-プロピル、酢酸*n*-ブチルの如き酢酸エステル類；メタノール、エタノール、1-プロパノール、2-プロパノールの如きアルコール類を挙げることができる。

【0034】上記分散液中には、ハードコート層の硬化触媒が通常含有される。硬化触媒としては、例えば、カルボン酸のアルカリ金属塩およびアンモニウム塩、アセチルアセトンの金属塩及びアンモニウム塩、エチルアセトアセテートの金属塩、及びアセチルアセトンとエチルアセトアセテートが配位した金属塩、第1～第3級アミン、ポリアルキレンアミン、スルホン酸塩、過塩素酸マグネシウム、過塩素酸アンモニウム等を挙げることができる。これらの化合物は有機メルカプタンやメルカプトアルキレンシランと併用することもできる。

【0035】上記金属塩の具体例としては、下記中心金属を含むキレート化合物あるいは脂肪族酸との塩類を挙げることができる。Al, Zr, Co, Zn, Sn, Mn, V, Cu, Ce, Cr, Ru, Ga, Cd, Feの如き中心金属；アセチルアセトン、ジ-*n*-ブトキシド-モノ-エチル アセテート、ジ-*n*-ブトキシド-モノ-メチル アセテート、メチルエチルケトオキシム、2,4-ヘキサジオン、3,5-ヘプタンジオン、アセトオキシムの如きキレート化合物；および2-エチル-ヘキシル酸、ステアリン酸、ラウリン酸、オレイン酸、酢酸、セバシン酸、ドデカン二酸、プロピオン酸、ブタジール酸、イソブチル酸、シトラコン酸の如き脂肪族酸化合物。

【0036】また、第1～第3アミンの具体例としては、脂肪族アミン、芳香族アミン、アミノシラン等が好ましく、例えば、ポリメチレンジアミン、ポリエーテルジアミン、ジエチレントリアミン、イミノビスプロピルアミン、ビスヘキサメチレントリアミン、ジエチレントリアミン、テトラエチレンペンタアミン、ペンタエチレンヘキサアミン、ペンタエチレンヘキサミン、ジメチルアミノプロピルアミン、アミノエチルエタノールアミン、メチルイミノビスプロピルアミン、メンタンジアミ

ン、*N*-アミノメチルピペラジン、1,3-ジアミノシクロヘキサノン、イソホロンジアミン、メタキシレンジアミン、テトラクロロパラキシレンジアミン、メタフェニレンジアミン、4,4'-メチレンジアニリン、ジアミノジフェニルスルホン、ベンジジン、トルイジン、ジアミノジフェニルエーテル、4,4'-チオジアニリン、4,4'-ビス(*o*-トルイジン)ジアニシジン、*o*-フェニレンジアミン、2,4-トルエンジアミン、メチレンビス(*o*-クロロアニリン)、ジアミニトリルスルホン、ビス(3,4-ジアミノフェニル)スルホン、2,6-ジアミノピリジン、4-クロロ-*o*-フェニレンジアミン、4-メトキシ-6-メチル-*m*-フェニレンジアミン、*m*-アミノベンジルアミン、*N*,*N*,*N'*,*N'*-テトラメチル-1,3-ブタンジアミン、*N*,*N*,*N'*,*N'*-テトラメチル-*p*-フェニレンジアミン、テトラメチルグアニジン、トリエタノールアミン、2-ジメチルアミノ-2-ヒドロキシプロパン、*N*,*N'*-ジメチルピペラジン、*N*,*N'*-ビス[(2-ヒドロキシ)プロピル]ピペラジン、*N*-メチルホルモリン、ヘキサメチレントトラミン、ピリジン、ピラジン、キノリン、ベンジルジメチルアミン、 α -メチルベンジルメチルアミン、2-(ジメチルアミノメチル)フェノール、2,4,6-トリス(ジメチルアミノメチロール)フェノール、*N*-メチルピペラジン、ピロリジン、ホルモリン、*N*- β (アミノエチル) γ -アミノプロピルトリメトキシシラン、 γ -アミノプロピルトリメトキシシラン、 γ -アミノプロピルトリエトキシシラン、*N*- β (アミノエチル) γ -アミノプロピルメチルジメトキシシラン、 γ -アミノプロピルメチルジエトキシシランを挙げることができる。

【0037】上記の如き硬化触媒は分散液の調合時でもあるいは塗布直前において添加することができる。硬化触媒の割合は、分散液中の有効固形成分に対し好ましくは0.001～10重量%である。

【0038】本発明において、シリコンハードコート層のための上記分散液は、後述する光触媒塗膜層の持つ余分な活性エネルギーが伝播して樹脂の劣化を促進する作用を回避する為に、該活性エネルギーを緩和する作用を有する化合物を含有するのが好ましい。

【0039】かかる化合物としては、例えばキレートの構造が脂肪族である金属キレート化合物や脂肪族酸金属塩の化合物が好ましく、ハードコート層のマトリックス樹脂に相溶性のあるものがさらに好ましい。

【0040】かかる化合物の中心金属としては、例えば、Co, Mn, V, Cu, Ce, Cr, Ru, Ga, Cd, Feを挙げることができる。また、キレート化合物としては、例えば、アセチルアセトン、ジ-*n*-ブトキシド-モノ-エチル アセテート、ジ-*n*-ブトキシド-モノ-メチル アセテート、メチルエチルケトオキ

シム、2,4-ヘキサンジオン、3,5-ヘプタンジオンおよびアセトキシシムを挙げることができる。さらに、脂肪酸化合物としては、例えば、2-エチルヘキシル酸、ステアリン酸、ラウリン酸、オレイン酸、酢酸、セバシン酸、ドデカン二酸、プロピオン酸、ブラシル酸、イソブチル酸、シトラコン酸を挙げることができる。これらの化合物のうち、400～550nmに吸収ピークを持ちそしてそれを含む溶液が青から赤紫色を呈するものが好ましい。

【0041】かかる化合物は、分散液中の固形分に対し0.001～5重量%で好ましく用いられる。0.001重量%より少ないとかかる化合物を使用した効果がほとんど得られずまた5重量%より多いとハードコート層の硬度が劣化しがちになる。

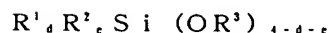
【0042】また、上記分散液は、任意成分として、硬化被膜のレベリング剤、潤滑性付与剤を含有することができる。かかる剤としては、例えばポリオキシアルキレンとポリジメチルシロキサンとの共重合体（ダウコーニング社のペイントアディティブ31）、ポリオキシアルキレンとフルオロカーボンとの共重合体が好ましく用いられる。かかる剤は、全液量に対して0.001～10重量%で好ましく使用される。その他任意成分として酸化防止剤、耐候性付与剤、帯電防止剤、ブルーイング剤等を含有することもできる。

【0043】上記分散液は、固形分濃度が例えば2～50重量%に調整されて好ましく用いられる。塗布は、例えばディップ法、フロー法、スピンナー法、スプレー法により行うことができる。

【0044】塗布は、硬化後の膜厚が2～7μmとなるような厚さで実施するのが好ましい。2μmより小さいと硬度が十分でなく、一方7μmより大きいとハードコート層にクラックが発生し易くなる。塗布後、分散液塗膜は例えば1～24時間、100～130℃の温度で加熱処理されることにより、シリコンハードコート層を与える。

【0045】本発明の被覆ポリカーボネート板は、シリコンハードコート層の上にさらに光触媒塗膜層を有する。かかる層は、光触媒効果を有する金属酸化物を含むシリコン樹脂からなる。光触媒効果を有する金属酸化物としては、紫外線照射により光触媒効果を発現するバンドギャップを生成する金属酸化物微粒子が好ましい。かかる微粒子としては、例えば、 TiO_2 、 TiO_3 、 $SrTiO_3$ 、 $FeTiO_3$ 、 WO_3 、 SnO_2 、 Bi_2O_3 、 In_2O_3 、 ZnO 、 Fe_2O_3 、 RuO_2 、 CdO 、 CdS 、 $CdSe$ 、 GaP 、 $GaAs$ 、 $CdFeO_3$ 、 MoS_2 、 $LaRhO_3$ 等を挙げることができる。好ましくは TiO_2 、 ZnO であり、特に好ましくはアナターゼ型 TiO_2 である。

【0046】また、シリコン樹脂としては、シリコンハードコート層について記載した下記式：



ここで、 R^1 、 R^2 、 R^3 、 d および e の定義は上記と同じである、で表される化合物の硬化物を好ましいものとして挙げることができる。

【0047】硬化触媒および液体媒体としてもハードコート等について記載したものと同じものを使用することができる。液体媒体としてはここでは特に1-プロパノールが好ましい。光触媒塗膜層のための塗液は固形分濃度が1～10重量%であるのが好ましい。

【0048】塗布は例えばディップ法、フロー法、スピンナー法、スプレー法により行うことができる。塗布は、硬化後の膜厚が5～50nmとなるような厚さで実施するのが好ましい。50nmより大きいと膜が白濁し、干渉色が見えるようになり好ましくない。塗布後、溶液塗膜は例えば1～5時間、100～130℃の温度で加熱処理されることにより、光触媒塗膜層を与える。

【0049】光触媒塗膜層はコロナ処理したシリコンハードコート層上に設けるのが好ましい。それによって、光触媒塗膜層は一層シリコンハードコート層に強く接合される。また、光触媒塗膜層には、ハードコート層について記載した化合物すなわち光触媒層の持つ余分な活性エネルギーが伝播して樹脂の劣化を促進する作用を回避する為に、該活性エネルギーを緩和する作用を有する化合物を含有させることができる。

【0050】本発明の被覆ポリカーボネート板は例えば防音壁、グレーディング用途、屋内用途に使用することができる。

【0051】

【発明の効果】上記のとおり、本発明によれば、長期間にわたり屋外で使用しても黄変がなく、曇りもない表面防曇性、防汚性を有した透明ハードコート付きポリカーボネート板を提供することができる。

【0052】

【実施例】以下、実施例により、本発明をさらに詳述する。実施例で用いた各種物質は次のとおりである。

ポリカーボネート板：ポリカエース（筒中プラスチック（株）製）厚み5mmの板（1m×30cm×5mm）を用いた。

【0053】プライマー1：メチルメタクリレートとメタクリロキシプロピルトリメトキシシランのモル比で4：1の共重合体（ $M_n=10000$ 、 $M_w=40000$ ）を100g、2,4-ジヒドロキシベンゾフェノン50g、プロピレングリコールモノメチルエーテルを850gとDow Corningペイントアディティブ31を0.1gからなる溶液。

【0054】プライマー2：アクリロイドA-10S（ローム&ハース社製のアクリル樹脂）100gと2,2',4,4'-テトラヒドロキシベンゾフェノン40g、プロピレングリコールモノメチルエーテルを860gとDow Corningペイントアディティブ31

を 0.1 g からなる溶液。

【0055】ハードコート1：スノーテックス0-40（日産化学製：コロイダルシリカ、水分散、不揮発分40%）150gとメチルトリメトキシシラン200gを反応させた後、イソプロピルアルコール648g、酢酸ナトリウム2g、Dow Corningペイントアディティブ31を0.1gを加えた溶液。

【0056】ハードコート2：スノーテックス0-40（日産化学製：コロイダルシリカ、水分散、不揮発分40%）150gとメチルトリメトキシシラン200gを反応させた後、2,4-ジヒドロキシベンゾフェノン20gとイソプロピルアルコール628g、酢酸ナトリウム2g、Dow Corningペイントアディティブ31を0.1gからなる溶液。

【0057】ハードコート3：スノーテックス0-40（日産化学製：コロイダルシリカ、水分散、不揮発分40%）150gとメチルトリメトキシシラン200gを反応させた後、イソプロピルアルコール647g、Co(I1)アセチルアセトン2水和物を0.1g、酢酸ナトリウム2g、Dow Corningペイントアディティブ31を0.1g加えた溶液。

【0058】TiO₂を含む溶液：ST-K03（石原産業製、不揮発分10%）を50wt%と1-プロピルアルコール50wt%からなる溶液。

【0059】また、実施例で用いた塗布方法等の条件および各種試験法は、以下のとおりである。

【0060】塗布方法：フローコートもしくはディップコート。

コロナ処理条件：出力500W、照射距離5mm、3分間処理。

ハードコート硬化条件：120℃で60分。

TiO₂を含む溶液の硬化条件：120℃で30-60分。

【0061】密着性：基盤め試験JIS K5400に準拠。

黄色度：JIS K7103に準じて測定。

硬さ：JIS K7204に準拠したテーバー磨耗試験で500g過重で500回転前後の濁度を比較。

濁度：JIS K7105に準拠。

初期の接触角：紫外線強度0.5mW/cm²の光源を30

時間照射した後の、0.1ccの水滴との接触角を測定。

耐候試験後の接触角：0.1ccの水滴との接触角を測定。

【0062】耐候性1：サンシャインカーボンアークウエザオメーター耐候促進試験機（ブラックパネル温度63℃、水スプレーを1時間当たり12分間噴霧）を用いて、3000時間後の外観、密着性を評価。

【0063】実施例1

ポリカーボネート板にプライマー1をフローコートで塗布硬化後（硬化後のプライマー層の厚さ1.8~3.5μm）、ハードコート1をフローコートで塗布硬化し（硬化後のハードコート層の厚さ2~5μm）、さらにコロナ処理後TiO₂を含む溶液を塗布硬化して、硬化後の光触媒塗膜層の厚みを20~40nmにした。

【0064】実施例2

プライマー2をフローコートで塗布硬化後（硬化後の厚さ1~2μm）、ハードコート2をフローコートで塗布硬化し（硬化後のハードコート層の膜厚2~5.5μm）、コロナ処理後TiO₂を含む溶液を塗布硬化して、硬化後の光触媒塗膜層の厚みを20~40nmにした。

【0065】実施例3

プライマー1をディップコートで塗布（引き上げ速度1.5m/分）し、115℃で30分間硬化後（硬化後のプライマー層の厚さ1.8~3.5μm）、ハードコート3をディップコートで塗布（引き上げ速度1.5m/分）し、120℃で60分間硬化し（硬化後のハードコート層の厚み2~5μm）、コロナ処理後TiO₂を含む溶液を塗布強化して、硬化後の光触媒塗膜層の厚みを20~40nmにした。

【0066】比較例1

実施例1においてコロナ処理後の工程を実施せず、その他は実施例1と同じに行った。

【0067】比較例2

実施例1において、ハードコート1を塗布硬化する工程を実施せず、その他は実施例1と同じに行った。結果を表1および表2に示した。

【0068】

【表1】

項目	初期性能				
	密着性	硬度	ヘイズ率	YI	初期接触角
実施例1	100%	2%	0.5%	-1.0	1°
実施例2	100%	4%	0.6%	0.1	1°
実施例3	100%	2%	0.6%	-1.5	1°
比較例1	100%	2%	0.2%	-1.0	85°
比較例2	100%	20%	0.4%	0.8	2°

【0069】

【表2】

項目	耐候性試験後				
	密着性	硬度	ヘイズ率	YI	接触角
実施例1	100%	4%	1%	1.0	6°
実施例2	100%	8%	2%	2.0	8°
実施例3	100%	4%	1%	0.5	3°
比較例1	100%	5%	1%	1.5	72°
比較例2	0%	20%	10%	18%	55°

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